

## **Bioinspired Chemistry for Energy: A Workshop Summary to the Chemical Sciences Roundtable**

Sandi Schwartz, Tina Masciangioli, and Boonchai Boonyaratanakornkit, Rapporteurs, Chemical Sciences Roundtable, National Research Council

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# BIOINSPIRED CHEMISTRY FOR ENERGY

## A WORKSHOP SUMMARY TO THE CHEMICAL SCIENCES ROUNDTABLE

Sandi Schwartz, Tina Masciangioli, and Boonchai Boonyaratanakornkit

Chemical Sciences Roundtable  
Board on Chemical Sciences and Technology  
Division on Earth and Life Studies

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\*These members of the Chemical Sciences Roundtable oversaw the planning of the Workshop on Bioinspired Chemistry for Energy but were not involved in the writing of this workshop summary.

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## Preface

The Chemical Sciences Roundtable (CSR) was established in 1997 by the National Research Council. It provides a science-oriented apolitical forum for leaders in the chemical sciences to discuss chemistry-related issues affecting government, industry, and universities. Organized by the National Research Council's Board on Chemical Sciences and Technology, the CSR aims to strengthen the chemical sciences by fostering communication among the people and organizations—spanning industry, government, universities, and professional associations—involved with the chemical enterprise. One way it does this is by organizing workshops that address issues in chemical science and technology that require national attention.

In May 2007, the CSR organized a workshop on the topic “Bioinspired Chemistry for Energy.” This document summarizes the presentations and discussions that took place at the workshop and includes poster presenter abstracts. In accordance with the policies of the CSR, the workshop *did not* attempt to establish any conclusions or recommendations about needs and future directions, focusing instead on issues identified by the speakers. In addition, the organizing committee's role was limited to planning the workshop. The workshop summary has been prepared by the workshop rapporteurs Sandi Schwartz, Tina Masciangioli, and Boonchai Boonyaratanakornkit as a factual summary of what occurred at the workshop.



## Acknowledgment of Reviewers

This workshop summary has been reviewed in draft form by persons chosen for their diverse perspectives and technical expertise in accordance with procedures approved by the National Research Council's Report Review Committee. The purpose of this independent review is to provide candid and critical comments that will assist the institution in making its published workshop summary as sound as possible and to ensure that the summary meets institutional standards of objectivity, evidence, and responsiveness to the workshop charge. The review comments and draft manuscript remain confidential to protect the integrity of the deliberative process. We wish to thank the following individuals for their review of this workshop summary:

**Kyu Yong Choi**, University of Maryland, College Park  
**Louis Graziano**, Rohm and Haas Company, Spring House, Pennsylvania  
**Paula T. Hammond**, Massachusetts Institute of Technology, Cambridge  
**Levi T. Thompson**, University of Michigan, Ann Arbor

Although the reviewers listed above have provided many constructive comments and suggestions, they were not asked to endorse the workshop summary nor did they see the final draft of the workshop summary before its release. The review of this workshop summary was overseen by **Jennie Hunter-Cevera**, University of Maryland, Rockville. Appointed by the National Research Council, she was responsible for making certain that an independent examination of this workshop summary was carried out in accordance with institutional procedures and that all review comments were carefully considered. Responsibility for the final content of this workshop summary rests entirely with the authors and the institution.



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# 1

## Overview—The Role of Bioinspired Chemistry in Improving Alternative Energy Technologies

Understanding the basic processes of photosynthesis and chemical conversion may enable scientists to create systems that mimic biomolecules and produce energy more efficiently. Some of the losses in photovoltaic energy conversion might be overcome with biomimetic processes.<sup>1</sup> Much work has been conducted in the development of artificial photosynthetic antennas, which provide rapid electron-transfer, as well as artificial reaction centers that generate a chemical potential by providing long-lived charged separation.<sup>2</sup> As in photosynthesis, light energy can be harvested to drive a sequential reaction in which water is oxidized to hydrogen (for the hydrogen economy) and oxygen.<sup>3</sup> Extensive progress has been made in catalyzing the formation of hydrogen from protons. Several catalysts have been developed to mimic hydrogenase activity.<sup>4,5</sup> However, a rate limiting step in water oxidation that remains to be overcome is the stitching together of oxygen atoms to form O<sub>2</sub> via bioinspired catalysts.<sup>6</sup>

In an effort to advance the understanding of “bioinspired chemistry for energy,” this workshop featured presentations, a poster session, and discussions on chemical issues by experts

from government, industry, and academia (see Appendix A for workshop agenda). Speakers at the workshop

- Summarized the current energy challenges, such as carbon emissions, population growth, and cost, and presented opportunities to address these challenges, such as developing sustainable energy sources.
- Provided an overview of the fundamental aspects and robust implementations of bioinspired chemistry from government, academic, and industrial perspectives.
- Explored the role of fundamental chemistry in biocatalysis applications for energy systems.
- Addressed how improvements in bioinspired catalysis might be harnessed for improved energy systems.
- Discussed the most promising research developments in bioinspired chemistry for energy systems.
- Identified future research directions.

### WORKSHOP STRUCTURE

The main speaker sessions are briefly described below. A more detailed summary of the speaker comments can be found in the chapters indicated in parentheses. The three main speaker sessions were:

1. Government, industry, and academic perspectives on bioinspired chemistry for energy (Chapter 2).
2. Fundamental aspects of bioinspired chemistry for energy (Chapter 3).
3. Robust implementation of bioinspired catalysis (Chapter 4).

In addition, two overarching themes were highlighted throughout the sessions: (1) partnership and integration (see

<sup>1</sup>LaVan, D. A. and J. N. Cha. 2006. Approaches for Biological and Biomimetic Energy Conversion. *Proceedings of the National Academy of Sciences* 103(14): 5251-5255.

<sup>2</sup>Gust, D., A. Moore, and T. Moore. 2001. Mimicking Photosynthetic Solar Energy Transduction. *Accounts of Chemical Research* 34(1): 40-48.

<sup>3</sup>Dismukes, C. 2001. Photosynthesis: Splitting Water. *Science* 292 (5516): 447-448.

<sup>4</sup>Liu, T. and M. Darensbourg. 2007. A Mixed-Valent, Fe(II)Fe(I), Diiron Complex Reproduces the Unique Rotated State of the [FeFe] Hydrogenase Active Site. *Journal of the American Chemical Society* 129(22): 7008-7009.

<sup>5</sup>Rauchfuss, T. 2007. Chemistry: A Promising Mimic of Hydrogenase Activity *Science* 316(5824): 553-554.

<sup>6</sup>Service, R. F. 2007. Daniel Nocera Profile: Hydrogen Economy? Let Sunlight Do the Work *Science* 315(5813): 789.

Chapter 5) and (2) research challenges, education, and training (see Chapter 6).

Opening remarks were made by **Douglas Ray**, Pacific Northwest National Laboratory followed by an overview perspective given by **John Turner**, National Renewable Energy Laboratory. Next, government perspectives on bioinspired chemistry for energy were presented by **Eric Rohlffing**, Office of Basic Energy Sciences Department of Energy; **Michael Clarke**, Chemistry Division, National Science Foundation; **Judy Raper**, Division of Chemical, Bioengineering, Environmental, and Transport Systems National Science Foundation; and **Peter Preusch**, National Institute of General Medical Science, National Institutes of Health.

The government perspectives were followed by industry perspectives on bioinspired chemistry for energy with presentations given by **Henry Bryndza**, DuPont; **Brent Erickson**, Biotechnology Industry Organization; and **Magdalena Ramirez**, British Petroleum. The overview session concluded with open discussion moderated by **Sharon Haynie**, DuPont.

The first technical session covered fundamental aspects of bioinspired chemistry for energy, and included the following topics and speakers: Hydrogen-Processing Catalysts for Replacement of Platinum in Fuel Cell Electrodes: Hydrogenases, **Marcetta Darensbourg**, Texas A&M University; The Lesson from the Hydrogenases? New Chemistry (Happens to Be Strategic), **Thomas Rauchfuss**, University of Illinois at Urbana-Champaign; Self-Assembly of Artificial Photosynthetic Systems for Solar Energy Conversion, **Michael Wasielewski**, Northwestern University and Argonne National Laboratory; and Sustained Water Oxidation by Bioinspired Catalysts: The Real Thing Now, **Charles Dismukes**, Princeton University. The talks were followed by open discussion, moderated by Sharon Haynie.

Speakers discussing fundamental aspects were asked to address the following questions: What are the design principles that enable biomolecular machines to effect selective and efficient atom- and group-transfer processes useful for energy conversions? What are the fundamental mechanisms of multi-electron transfer in biological systems? What are the principles of energy storage and production in biology? How do biological systems such as catalysts composed of seemingly fragile peptide residues achieve durability and robustness?

The technical session on fundamental aspects of bioinspired chemistry for energy concluded with remarks by Sharon Haynie, followed a poster session in which students and junior researchers presented emerging ideas in the realm of bioinspired chemistry for energy. Abstracts for the poster presenters are in Appendix C. The first day of the workshop adjourned after the poster session.

Day two of the workshop opened with remarks by **Leonard Buckley**, Naval Research Laboratory, followed by the academic perspective on bioinspired chemistry, Solar Fuels: A Reaction Chemistry of Renewable Energy presented by **Daniel Nocera**, Massachusetts Institute of Technology.

Next, there was a technical session on robust implementation of bioinspired catalysts, which included the following topics and speakers: Mimicking Photosynthetic Energy Transduction, **Thomas Moore**, Arizona State University; Biological Transformations for Energy Production: An Overview of Biofuel Cells, **G. Tayhas Palmore**, Brown University; and Bioinspired Initiatives at DuPont, **Mark Emptage**, DuPont. Open discussion was then moderated by Leonard Buckley.

Speakers addressing robust implementation responded to the following questions: How can bioinspired design principles be replicated in synthetic and semisynthetic catalysts and catalytic processes? Can discovery methods (e.g., bioinformatics) be harnessed to encode designer catalytic sites? To what extent can protein scaffolds be replicated with more easily synthesized supports, and can we use these principles to design sequential catalytic assemblies?

The workshop concluded with remarks by Leonard Buckley.

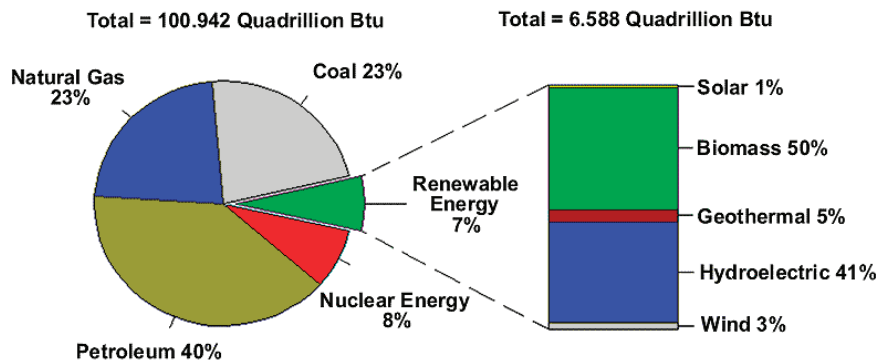
## OPENING REMARKS

**Douglas Ray** of the Pacific Northwest National Laboratory welcomed about 75 workshop participants and provided some initial thoughts on the energy crisis and how chemistry can play a role. With about 86 percent of energy currently coming from coal, gas, and oil, and only 7 percent from renewables (mostly conventional hydroelectric and biomass; see Figure 1.1),<sup>7</sup> Ray noted it is important to consider whether renewables, such as solar energy, hydrogen fuel, and biofuels, could reach the necessary scale needed to support current energy demand. He questioned whether our quality of life would be affected by the energy sources used. Ray also explained that progress in the energy field will depend on how scientists shape the future. He explained that transformational science—which focuses on translating what can be learned from biology to energy issues—is critical for changes to take place.

## Workshop Charge

Ray then motivated the workshop participants to take advantage of this opportunity to reach across disciplines and learn from one another. He hoped that the workshop discussion would bring together traditional scientific disciplines to identify new science directions. Ray talked about what can be learned from biology and how that knowledge can be translated into more robust applications through chemistry. The forum was an opportunity to create new understanding and identify a research agenda for the future. Ray concluded

<sup>7</sup>Energy Information Agency. 2007. *Renewable Energy Annual, 2005 Edition*. Table 1. [http://www.eia.doe.gov/cneaf/solar/renewables/page/rea\\_data/rea\\_sum.html](http://www.eia.doe.gov/cneaf/solar/renewables/page/rea_data/rea_sum.html) (accessed 11/16/07).



**FIGURE 1.1** The role of renewable energy consumption in the nation's energy supply, 2005.

SOURCE: Energy Information Agency. 2007. *Renewable Energy Annual, 2005 Edition*. Table 1. [http://www.eia.doe.gov/cneaf/solar.renewables/page/rea\\_data/rea\\_sum.html](http://www.eia.doe.gov/cneaf/solar.renewables/page/rea_data/rea_sum.html) (accessed 11/16/07).

his presentation with the following questions to keep in mind during the workshop:

- How do we organize bioinspired systems to effectively manage charge transport, electron transfer, proton relays, and allow efficient interconversion of light and electrical charge?
- How are the properties of bioinspired systems affected when they are coupled with interfacial and nanoscale systems?
- How do we control the properties and architectures of biomolecular systems and materials?
- What role do weak interactions play in self-assembly of molecular and nanostructured materials?

## SETTING THE STAGE: OPPORTUNITIES AND CHALLENGES FOR ENERGY PRODUCTION

**John Turner** of the National Renewable Energy Laboratory provided background information about energy to serve as a basis for the rest of the workshop discussions. "Energy is as important to modern society as food and water. Securing our energy future is critical for the viability of our society. Time is of the essence and money and energy are in short supply," said Turner. He estimated that 73 million tons of hydrogen per year for light-duty vehicles (assuming 300 million vehicles, and 12,000 miles per year) and 27 million tons of hydrogen per year for air travel would be needed to meet the current energy demand in the United States.

With world population growing at a fast pace, the demand for energy grows, especially in developing nations, noted Turner. He commented that the United States needs to be concerned about energy usage in developing nations. He mentioned a quote by C. R. Ramanathan, former Secretary, Ministry of Non-Conventional Energy Sources, Government of India: "Energy is the major input of overall social-economic development." According to Turner, the United

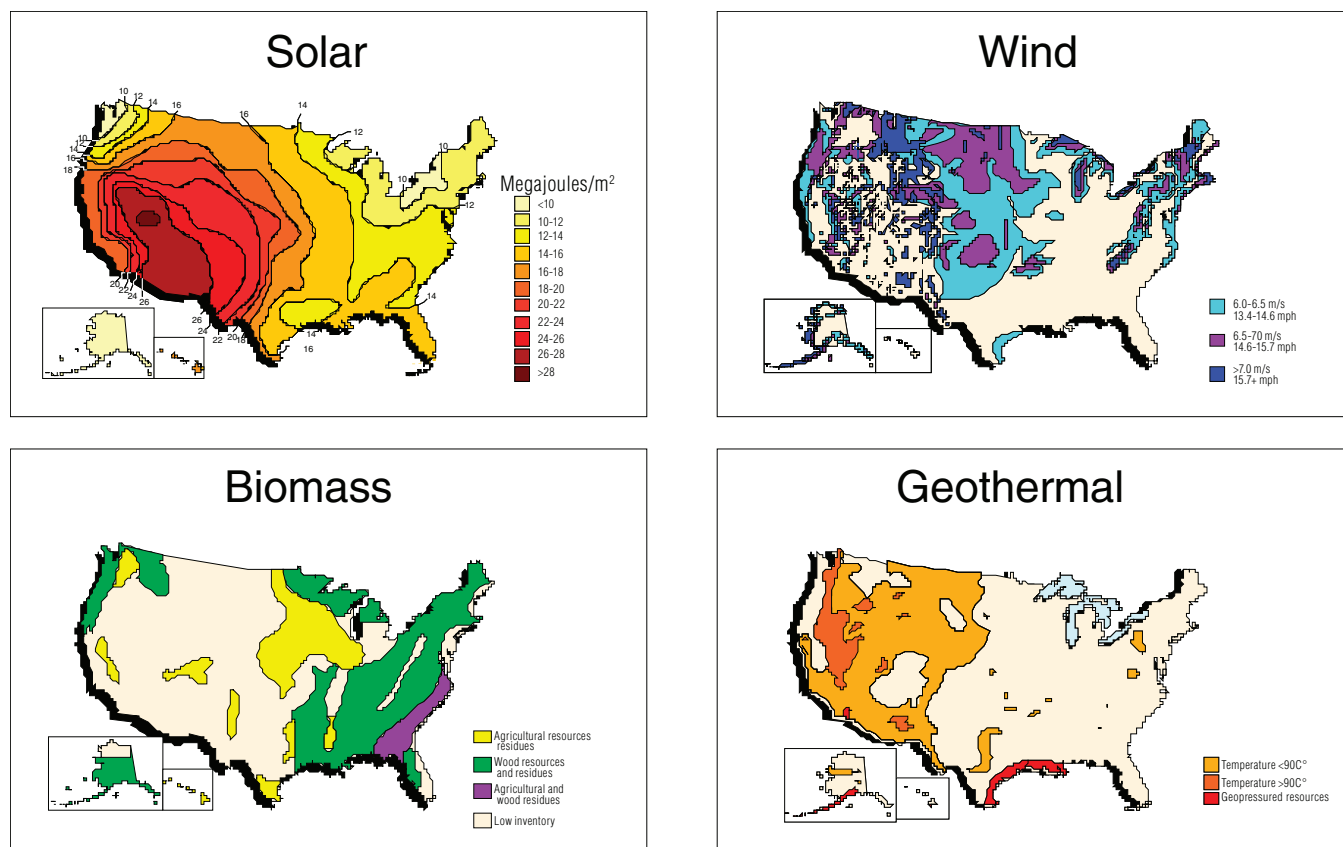
States will need to provide the energy-generating technologies developed in this country to the developing nations in order for their standard of living to increase. Historically, as the standard of living for a country increases, the population growth rate decreases, said Turner.

Realizing that the current energy system is expected to last for only 200-250 years, Turner posed the question: "What energy-producing technologies can be envisioned that will last for millennia and can be implemented in developing countries?" He explained that renewable energy systems—including biomass, solar, wind, geothermal, nuclear (fusion), hydro, wave, and hydrogen—will meet these needs because of sustainability, resource availability, and energy payback criteria. Figure 1.2 shows the solar, wind, biomass, and geothermal energy resources available in the United States.

## Hydrogen

Turner highlighted hydrogen because it plays a role in every fuel available and is a potential sustainable fuel on its own. He provided his own definition of a hydrogen economy: "The production of hydrogen, primarily from water but also from other feedstocks (mainly biomass), its distribution, and its utilization as an energy carrier." Turner explained that the goal is to develop the hydrogen economy so that it can be used for transportation and energy storage and back up intermittent sustainable resources, such as solar and wind. Feedstocks, including water, fossil fuels, and biomass, can produce hydrogen through a number of pathways, including electrolysis, thermolysis, and conversion technologies. Biomass feedstocks can comprise crop residues, forest residues, energy crops, animal waste, and municipal waste, and, according to Turner, could have the potential to provide 15 percent of the world's energy by 2050.<sup>8</sup> Some challenges

<sup>8</sup>Fischer, G. and L. Schrattenholzer, 2001. Global Bioenergy Potentials Through 2050. *Biomass and Bioenergy* 20: 151-159.



**FIGURE 1.2** Geographic distribution of U.S. sustainable energy resources: Solar, wind, biomass, and geothermal.  
 SOURCE: Presented by John Turner, National Renewable Energy Laboratory.

with this option include biomass availability, cost, and physical and chemical properties. Biomass can provide significant energy, but, said Turner, it is important to remember that its main role is to be a food source and it can also be an important chemical feedstock to replace fossil-based feedstocks.

Turner then explained how electrolysis is a commercial process that produces hydrogen by splitting water using electricity. This commercial technology can generate hydrogen as an energy carrier using sustainable energy resources, such as wind and PV, which directly generate electricity. Turner warned of the challenges with some electrolysis technologies involving the use of platinum group metals, largely due to the high price of these metals (about \$1,300 an ounce or \$46 a gram for platinum, according to Turner). Thermochemical water-splitting cycles handle chemicals and materials under conditions that challenge the current state of the art for construction materials and heat transfer fluids. For solar energy, such infrastructure needs also include solar reflectors and thermal storage. Turner does not think that thermochemical cycles should be a high priority because they are extremely challenging and these thermal-based systems are probably better used to produce electricity.

Direct conversion systems use the energy of visible light to split water into hydrogen and oxygen. Combining light harvesting and water-splitting systems into a single system uses semiconductor, photoelectrolysis, and photobiological systems. According to Turner, the sustainable paths to hydrogen are:

Solar energy → heat → thermolysis → hydrogen  
 Solar energy → biomass → conversion → hydrogen  
 Solar energy → electricity → electrolysis → hydrogen  
 Solar energy → photolysis → hydrogen

### Growth Rates and Payback

Turner emphasized the importance of growth rates for technology deployment and energy demand. New energy technologies can be a significant challenge but also a benefit, depending on the technology. Turner noted that the worldwide demand for energy continues to grow. Thus, alternative technologies must grow at high rates in to have an impact. The installation of wind farms, for example, is growing quickly; in fact, wind energy has a 27 percent average

TABLE 1.1 Energy Payback Comparisons for PV and Wind

Technology	Lifetime	Payback	Payback ratio
Solar: Crystalline and thin film photovoltaic cells (includes frames and supports)	30 years	2-3 years	10
Wind: fiberglass blade turbines (includes mechanical parts and scrapping the turbine at the end of its life)	20 years	3-4 months	20

SOURCE: Presentation by John Turner, National Renewable Energy Laboratory.

growth rate in the United States, says Turner. Although wind currently supplies less than 1 percent of electricity, Turner suggested that its high growth rate would quickly increase its market share. If wind could maintain that 27 percent growth rate, Turner thinks that by 2020 the kilowatt hours from wind could surpass that generated from current U.S. nuclear power plants. In 2005, production of photovoltaics (PV) rose by 47 percent, which is indicative of world demand. If PV could maintain a growth rate of 30 percent, Turner said PV production would rise to 1 TW per year (peak) in 2028, but because of the steady increase in demand, this would only represent 10 percent of electricity needs. He pointed out that any technology that hopes to address carbon-free energy needs should be on the ground now and maintain close to a 30 percent growth rate for the next 20 years to have an impact. Because coal with carbon capture and storage will take years to get on ground, it may be too late to make a significant contribution to future carbon-free energy systems. “If we want a change in the energy infrastructure in the next 50 years or so, we have to start and maintain these large growth rates in alternative energy technologies,” said Turner.

He stated that energy payback—a net gain in energy—is another important consideration when choosing the best energy resource. Turner believes that any system without net energy payback will eventually be replaced by another energy system. Positive net energy occurs only with energy systems that are converting energy from outside the biosphere, said Turner—such as for solar (PV) and wind (see Table 1.1). However, he added that for PV, growth rates above 35 percent require a large energy input (e.g., to produce the technology), and this leads to an overall negative energy balance (net loss of energy). Turner noted that wind is better in this respect, because it still provides an energy payback even at a 40 percent growth rate.

Cost

Fuel costs for transportation was another issue raised in Turner’s presentation. In the United States, gasoline is currently about \$3/gallon, which is 12¢/mile for a 25-mile-per-gallon vehicle. A National Renewable Energy Laboratory study has shown that at today’s costs a large wind farm coupled to a large electrolyzer plant can produce hydrogen at a cost of about \$6/kg at the plant gate. If that hydrogen is used in a fuel-cell vehicle with a fuel economy of 50 miles per kilogram, that hydrogen as a transportation fuel is also

12¢/mi. Therefore, concluded Turner, hydrogen is on par with gasoline, and it should not cost much more to implement it on a larger scale.

He also made a note of future water issues that may need to be addressed if hydrogen from water electrolysis is used more frequently. One hundred billion gallons of water per year will be required for the U.S. hydrogen-fuel-cell vehicle fleet. On the other hand, wind and PV consume no water during electricity production, and thermoelectric power generation utilizes only about 0.5 gallon of water for every kilowatt-hour produced. If wind and solar are aggressively installed, overall water use will decrease, said Turner.<sup>9</sup>

Vision for the Future

Turner compared renewable energy and coal with carbon sequestration and explained that he prefers a renewable energy source because coal resources are finite and it takes energy to sequester carbon. To modify or build a new energy infrastructure requires money and energy—and that energy must come from existing resources.

Turner’s vision for the pathway to the future includes promotion of renewable energy, developing fuel cells for transportation (hydrogen initially from natural gas), implementing large-scale electrolysis for hydrogen production as sustainable electricity increases, and increasing funding for electrocatalysis. He concluded with: “We have a finite amount of time, a finite amount of money, and a finite amount of energy, and we need to be very careful about the choices we make as we build any new energy infrastructure. I’d like to see something that will last for millennia, and certainly solar, wind, and biomass will last as long as the sun shines.”

DISCUSSION

Following Turner’s presentation, some workshop participants provided their own thoughts and asked questions of the speaker. **Daniel Nocera** followed up on Turner’s comments about energy scale. Nocera said that if a new material or new bioinspired approach can be done cheaply, there will not be the growth rate penalty for PV (above a 35 percent

<sup>9</sup>For more information, see the recent NRC workshop summary on “Water Implications for Biofuels Production.” Soon to be released at [www.nap.edu](http://www.nap.edu).



growth rate) that Turner mentioned earlier. Scientists can create new technologies to improve the energy payback, according to Nocera. Turner agreed, and said that scientists need to find less energy-intensive ways to make energy conversion systems, while also maintaining the growth rate. The quicker that more efficient, less expensive materials and systems are identified, the easier society can move to a sustainable energy system.

**Frankie Wood-Black** of ConocoPhillips mentioned that there can be unintended consequences of new energy systems and that scientists will need to consider these potential unintended consequences when new technologies are being developed. She used hydrogen and electric cars as an example. Since those vehicles are much quieter than vehicles with traditional combustion engines, pedestrians do not hear them and are at risk of being involved in an accident.

**Charles Casey** of the University of Wisconsin brought up concerns about hydrogen as an energy carrier because of infrastructure challenges. He suggested that hydrogen be converted into hydrocarbons since the infrastructure is already available for hydrocarbons. Turner responded by stating that the infrastructure really does not exist for synthesis of these proposed hydrocarbons. Carbon dioxide would have to be taken out of the air and added to hydrogen in order to generate a fuel, which is a huge challenge in the United States, said Turner. He argued that a hydrogen infrastructure does indeed exist since 9 million tons of hydrogen is produced every year in the United States. The hydrogen infrastructure is just not in a form that is recognized.

## 2

# Government, Industry, and Academic Perspectives on Bioinspired Chemistry for Energy

During three different sessions of the workshop, government, industry, and academic representatives presented perspectives on bioinspired chemistry for energy. Representing the federal government were Eric Rohlffing of the U.S. Department of Energy's (DOE's) Office of Basic Energy Sciences; Michael Clarke of the National Science Foundation's (NSF's) Chemistry Division; Judy Raper of NSF's Division of Chemical, Bioengineering, Environmental and Transport Systems; and Peter C. Preusch of the National Institutes of Health's (NIH's) Pharmacology, Physiology, and Biological Chemistry Division. The industry perspective was provided by Henry Bryndza of DuPont, Brent Erickson of the Biotechnology Industry Organization, and Magdalena Ramirez of British Petroleum (BP). Daniel Nocera from the Massachusetts Institute of Technology discussed the issue from an academic point of view.

### GOVERNMENT PERSPECTIVE

**Eric Rohlffing**, DOE, discussed the bioinspired chemistry for energy work being done in the agency's Office of Basic Energy Sciences (BES). The office funds basic research that will lead to revolutionary discoveries to address energy issues. He categorized the work being done into three broad areas, although he did not go into detail about the third since it is not in the division he manages. The overall theme of these areas is to learn from nature but also to figure out how to accomplish tasks more quickly.

1. Learning how to convert sunlight into chemical fuels like nature does, only better.

- Detailed studies of the molecular mechanism of natural photosynthesis to create artificial systems that mimic some of the remarkable traits of natural ones (i.e.,

self-assembly, self-regulation, and self-repair) while improving efficiency.

- Work encompasses light harvesting, exciton transfer, charge separation, redox chemistry and uses all the tools of the modern physical sciences in conjunction with molecular biology and biochemistry.

2. Learning catalysis tricks from nature.

- Apply lessons learned from natural enzymes to the design of organometallic complexes and inorganic and hybrid solids that catalyze pathways with unique activity and selectivity.

- Characterize the structure and dynamics of active sites in enzymes and the correlated motions of secondary and tertiary structures. Measure half-lifetimes of individual steps of electron- and ion-transport during catalytic cycles. Synthesize ligands for metal centers and functionalize inorganic pores to attain enzyme-like activity and selectivity with inorganic-like robustness.

3. Learning from nature about how to make novel materials.

- Emphasis on the merger of biological and inorganic systems at the nanoscale.

Rohlffing presented an organizational chart of the Chemical Sciences, Geosciences, and Biosciences Division, which he manages. He pointed out the four programs in the division that are working on bioinspired chemistry for energy: Solar Photochemistry, Photosynthetic Systems, Physical Biosciences, and Catalysis Science. The goal of these programs is to define and understand the structure, biochemical composition, and physical principals of natural photosynthetic energy conversion.

A major research goal of BES is to figure out how photosynthesis works and then design artificial or biohybrid



systems that directly produce solar fuels better than plants do to avoid having to use plants. Rohlfling presented three examples of research sponsored by BES that demonstrate how chemistry relates to dynamics and change.

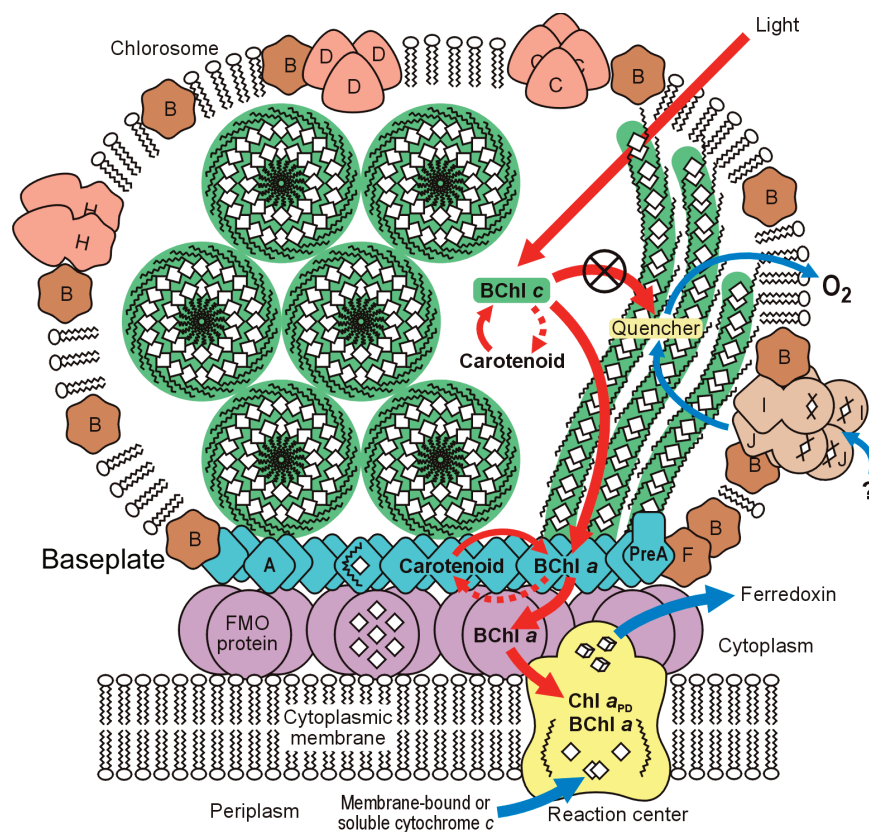
First, the Fenna-Matthews-Olson, or FMO, complex is a bacteria-chlorophyll complex that acts as a photosynthetic system (Figure 2.1). It is a conduction device for transporting the electrical energy when harvesting light. Researchers are trying to determine how energy is transferred along the set of chlorophylls. Is it by energy hopping or is there some more complex physical process? Coherent spectroscopy based on a femtosecond photon-echo technique in the visible region of the spectrum was applied to the FMO complex to determine whether there is quantum coherence (quantum beats) in the system. Quantum coherence is important because it helps avoid kinetic traps, explained Rohlfling.

The second example of research being funded by DOE involves a model system, metalloporphyrin, which looks at excited-state evolution using time-resolved X-rays. This research sets the groundwork for future research that will be conducted on much shorter time scales than the femtosecond domain.

The third research project presented by Rohlfling looked at the intrinsic motions of proteins as they influence catalysis and enzymes. Characterizing the intrinsic motions of enzymes is necessary to fully understand how they work as catalysts. As powerful as structure-function relationships are, the motion of these proteins is intimately connected with their catalytic activity and cannot be viewed as static structures. This realization, asserted Rohlfling, could revolutionize and accelerate approaches to biocatalyst design or directed evolution, and could alter understanding of the relations between protein structure and catalytic function.

The next speaker was **Michael Clarke** of NSF's Chemistry Division. He explained that the NSF funds a broad range of science and that the agency is concerned about making energy sustainable and solving the carbon dioxide problem.

Next he discussed the method that NSF uses to fund the scientific research. It has a program that was originally called the Chemical Bonding Centers but is now morphing into Centers for Chemical Innovation, which makes a number of relatively small awards, around \$500,000, to fund groups of



**FIGURE 2.1** Model of the photosynthetic apparatus (Fenna-Matthews-Olson complex) in *Chlorobium tepidum*.  
 SOURCE: Donald A. Bryant, The Pennsylvania State University, and Dr. Niels-Ulrik Frigaard, University of Copenhagen.

scientists who collaborate in addressing a major chemistry problem. For example, Harry Gray, Kitt Cummins, Nate Louis, Dan Nocera, and others are working on a project involving the direct conversion of sunlight into fuel. They are in the initial stages of the program and have received about \$500,000 so far. After several years, the research teams can apply for funding of several million dollars per year. Other similar research projects being funded by NSF (detailed below) focus on carbon dioxide, photochemical physics of charge separation, and finding a way to organize supramolecular structures in various ways using weak bonds, hydrogen bonds, and covalent bonds.

### Carbon dioxide

- Marcetta Darensbourg, Texas A&M University: Looking at carbon-carbon coupling reactions as mediated by transition metals. The nickel sites serve as the catalyst.
- Geoffrey Coates, Cornell University: Using a solid-state catalyst to incorporate carbon dioxide into polycarbonates.
- Donald Darensbourg, Texas A&M University: Pioneered the use of metal catalysts for converting the nontoxic, inexpensive carbon dioxide and three-membered cyclic ethers (epoxides) to thermoplastics, which are environmentally friendly and productively use greenhouse gas emissions. He is also working on developing effective nontoxic metal catalysts for producing a biodegradable polycarbonate from either trimethylene carbonate or trimethylene oxide and carbon dioxide.
- Janie Louie, University of Utah: Using platinum and nickel catalysts that allow carbon dioxide to be used as a starting material for organic synthesis.

### Photochemical physics of charge separation

- Dmitry Matyushov, Arizona State University: Using a ferroelectric medium to facilitate charge transfer since the main cause of inefficiency of current artificial photosynthesis

is fast charge recombination following photoinduced charge transfer. This research has succeeded in reducing the recombination rate.

- Francis D'Souza, Wichita State University: This research is focused on using assembled nanosystems to separate charges and facilitate transfer, and involves an interdisciplinary team of researchers (Figure 2.2).

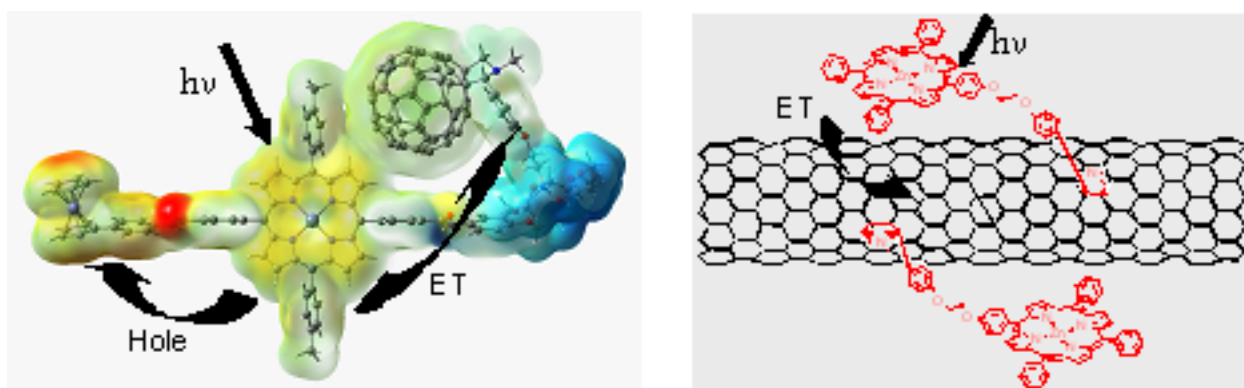
### Finding a way to organize supramolecular structures in various ways using weak bonds, hydrogen bonds, and covalent bonds

- Dan Reger, University of South Carolina: Using water to organize organic molecules into a nanostructure.
- Clarke said that finding a way to organize supramolecular structures needs to be done in order to affect charge transfers. Forming fuels are synthesized by using all of the types of bonding that chemists have available to them to bring together the various components in organized structures, noted Clarke.

**Judy Raper** of NSF's Division of Chemical, Bioengineering, Environmental and Transport Systems explained how NSF takes a broad view of bioinspired chemistry. Some of the main areas that NSF focuses on are:

- Bioinspired nanocatalysis for energy production that involves using starch (corn) or cellulose (wood) to produce renewable fuels and chemicals.
- Bioinspired hydrogen production.
- Production of liquid biofuels (both ethanol and alkanes).
- Microbial fuel cells.

Raper explained that NSF programs support the following bioinspired chemistry for energy research under the National Biofuels Action Plan: metabolic engineering, plant genome research, catalysis and biocatalysis, biochemical



**FIGURE 2.2** Supramolecular nanostructures for light driven energy and electron transfer. This research is focused on rational design and study of self-assembled porphyrin, fullerene, and carbon nanotube bearing supramolecular complexes and nanostructures.

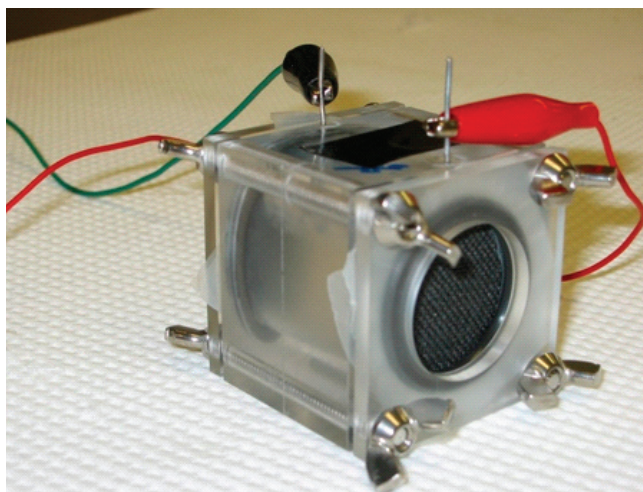
SOURCE: Presented by Michael Clarke, National Science Foundation; used with permission from Francis D'Souza, Wichita State University.

and biomass engineering, biotechnology, energy for sustainability, environmental sustainability, and organic and macromolecular chemistry. She highlighted some of the currently funded NSF projects.

In the area of bioinspired catalysis, Raper mentioned the work of a few researchers. Dennis Miller and James Jackson at Michigan State are exploring taking starch or cellulose, extracting the carbohydrate, and fermenting it to organic acid and glycerols. Robert Davis at the University of Virginia is looking at gold nanoparticles as catalysts for the conversion of glycerol to glyceric acid.

Raper also highlighted work in the area of bioinspired hydrogen production and microbial fuel cells. David Dixon at the University of Alabama is studying photocatalytic production of hydrogen. Bruce Logan of Pennsylvania State University is looking at hydrogen production by fermentation of waste water (as well microbial fuel cells for energy production; Figure 2.3). Dianne Ahmann at the Colorado School of Mines is using Fe-hydrogenase to produce commercial algal hydrogen. Lars Angenent of Washington University Nonfermentable products in wastewater are being used to produce electricity in microbial fuel cells.

NSF also supports production of liquid biofuels. James Dumesic at the University of Wisconsin is looking at green gasoline, which involves using inorganic catalysts to make alkanes, jet fuels, and hydrogen. Dumesic is breaking up cellulose to make aqueous phase reforming through syngas for alkane products, hexane, and through hydroxymethylfurfural to make jet fuels or polymers. Ramon Gonzales at Rice University is exploring anaerobic fermentation of glycerol in *E.coli* for biofuels production.



**FIGURE 2.3** Power Generation with Microbial Fuel Cells.  
SOURCE: Presentation of Judy Raper, National Science Foundation; used with permission from Bruce Logan, Pennsylvania State University.

**Peter C. Preusch** of the Pharmacology, Physiology, and Biological Chemistry Division of the National Institute of General Medical Sciences at the NIH discussed the agency's mission and how bioinspired chemistry for energy fits into it. The mission of NIH is to pursue fundamental knowledge about the nature and behavior of living systems and the application of that knowledge to extend healthy life and reduce the burdens of illness and disability. That mission, asserted Preusch, has allowed interesting dual-use science to be supported that is relevant to both basic energy research and human health. NIH has a large budget but nothing earmarked for research in this area. The National Institute of General Medical Sciences is one of the largest supporters of chemical sciences research in the nation, said Preusch.

The bioinspired chemistry research that has been supported by NIH falls into two categories: (1) chemical models of biological processes for the purpose of better understanding those biological processes and (2) using chemistry that is related to biology or using biological catalysts to accomplish chemical processes at a scale that is industrially significant.

Preusch provided examples of investigator-initiated grant-based projects funded by NIH that address fundamental physical processes and reactions of elements that are important in both global energy cycles and human health. Note that NIH has not solicited proposals in this area, but has supported a considerable amount of research that reflects investigator-initiated ideas in the field.

- **Energy transfer:** How light energy is captured, transmitted from an initial absorbing molecule through a series of intermediate molecules to a site at which that energy is captured in the form of electron-proton separation across a membrane.
- **Electron transfer:** Basic to the function of the respiratory chains of mitochondria and bacterial pathogens.
- **Oxygen activation:** Work on mimics of cytochrome P450 to understand how they function and use catalysts in order to activate molecules for oxygen insertion and to activate oxygen.
- **Oxygen reduction:** Models have been created for cytochrome oxidase, which have provided insights into the oxygen activation and reduction mechanism.
- **Hydrogen peroxide:** Model studies on catalases, peroxidases, and superoxide dismutases have provided insights into biological protection against oxidative damage.
- **Hydrogen reduction:** Model studies of hydrogenase provide insights relevant to the pathogenic organism *Helicobacter pylori* and its ability to survive in the gastric mucosa.
- **Nitrogen oxide production and reduction:** Relevant to the production and disposal of nitrogen oxides as signaling molecules and biological responses to environmental nitrogen oxides.
- **Nitrogen reduction:** Nitrogenase has been a model system for studying general principles involving electron



transfer, energy coupling, fundamental structures of metal complexes, and the chemical control of their assembly.

At the end of his talk, Preusch described the grant application and award process for regular research grants, conference grants, and academic research enhancement awards.

## INDUSTRY PERSPECTIVE

**Henry Bryndza** of DuPont began his presentation by emphasizing how expansive the subject area of this Bioinspired Chemistry for Energy workshop can be, stating, “When I think about ‘bioinspired,’ it means everything from biomimetics to superior process technology for bioprocesses, through integrated science approach, to even the production of chemicals and materials that are enabled by an emerging infrastructure in renewably available feedstocks. Similarly, when you’re talking about ‘energy,’ it’s not only energy production in terms of conventional sources that are in widespread use today but also so-called alternative or renewable energies.” He also said that recycling and use minimization should be considered in the overall energy picture.

Bryndza believes that a tipping point has been reached in the drive for alternative energy sources and that they offer significant potential for future growth. The success or failure of alternative energy sources, claimed Bryndza, has major implications for the United States as well as for the planet in terms of political climate, environmental performance, and economic health. He believes it is unlikely that there will be one global solution; rather, he thinks there are going to be local minima that are dictated, in part, by availability and cost of technology and its capital intensity. The availability and cost of feedstocks vary by region, and different governments have different subsidies, regulations, incentives, and policies that will also drive the local minima for fast adoption.

Bryndza explained how DuPont is a science company that is heavily dedicated to the energy market and sustainable growth. He talked about the company’s sustainability policies that were established in 1989 and updated in 2006. By 2010, Bryndza estimated 25 percent of revenues from DuPont’s businesses are expected to be derived from operations using raw materials that are not depleted, and 10 percent of the company’s energy needs will be derived from renewable sources.

Bryndza then touched on the selection criteria that DuPont uses to decide which projects to undertake. Projects must be consistent with the corporate vision and sustainability principles, unique, multigenerational, consistent with DuPont competences, have a valid route to market, and DuPont’s stake needs to be large enough to justify the effort.

DuPont is already heavily invested in products, services, and research in support of global energy markets as diverse as petrochemicals, fuel cells, photovoltaics, and biofuels. The company supplies products to the sugar- and corn-based

ethanol industries. Offerings under development from biomass feedstocks include improved biomass to energy, crop protection chemicals, and cellulosic ethanol and butanol technologies coming from biorefineries.

Biomass includes a range of materials from simple plant oils and sugars that can be converted into liquid transportation fuels to cellulose, hemicellulose, and lignocellulose which are successively much harder to address. Bryndza explained that there are many potential conversion processes that deliver energy in different ways, ranging from distributed power or stationary power to liquid transportation fuels. DuPont is working on a number of different conversion processes and trying to identify the most efficient ones. The cellulosic ethanol program is a consortium effort involving other companies, government laboratories, and academia. The project is looking at a variety of chemical and biological technologies to convert biomass into useful products ranging from fuels to chemicals and materials. DuPont thinks that the variation in biomass feedstocks will require an integration of sciences and multiple technologies.

Bryndza believes that integration is important to finding the best solution to the world’s energy crisis. If scientists approach energy problems from either a biological perspective or a chemical perspective, asserted Bryndza, alternative energy technologies will not work economically. He said, “We really need partnerships. . . . We are partnering in virtually all of these areas for a couple of reasons. One is that we can’t do it all ourselves. The second is that, in some cases, partners bring technology or access to markets that we don’t have.”

**Brent Erickson** of the Biotechnology Industry Organization (BIO) said his organization is the world’s largest trade association, with over 1,000 member companies in 33 countries. It represents the gamut of biotechnology from health care to food and agriculture biotech to industrial and environmental biotech. According to Erickson, pharmaceutical and agriculture areas are already well developed, so the next wave is fuels, chemicals and manufacturing, biopolymers, chiral intermediates, and products for farm and fine chemicals. BIO advocates on Capitol Hill are currently trying to gain support from policy makers for biorefinery development.

Erickson provided several reasons why industrial biotech is important for innovation and commercialization:

- Because process innovation is slowing, the chemical industry must identify new places to find innovation.
- Energy prices and availability of petroleum-based feedstocks are problematic.
- The global marketplace is becoming increasingly competitive.
- Industrial biotech is advancing rapidly, providing new tools for innovation, cost reduction, and improving environmental performance.

Industrial biotech represents a broad range of applications, including biobased products, bioenergy, biobased polymers, and national defense. The Department of Defense, for example, has a program to build mobile biorefineries that recycle kitchen waste.

Erickson's vision for the future includes creating a biobased economy in which the basic building blocks for industry and raw materials for energy are derived from renewable plant sources and are processed using industrial biotechnology. According to Erickson, technologies should be developed that go beyond a simple starch-to-ethanol platform that exists now.

Erickson believes that industrial biotechnology is attractive to business because it can decrease production costs and increase profits, increase the sustainability profile, allow for broader use of renewable agricultural feedstocks instead of using petroleum, and provide precision catalysis. However, he thinks industrial biotechnology can also be disruptive as it converges with other scientific disciplines because of its shorter research and development cycles. Erickson then discussed the importance of partnership among companies, which is detailed in Chapter 5.

So how will the biobased economy actually happen? Erickson believes that radically new business models will appear that challenge traditional companies, but unique opportunities for the fast movers will be created. Companies that are early adopters of industrial biotech will gain a competitive advantage in the marketplace, said Erickson.

What is the market potential? Industrial biotech is already 5 percent of global chemical production, and Erickson believes it will continue to accelerate rapidly. McKinsey and Company estimates that by 2010 industrial biotech could be worth \$280 billion.

In conclusion, Erickson stated that, "industrial biotech and biological chemistry are really at the right place at the right time with the right tools to make a big difference in our energy security, our economy, and our environment."

**Magdalena Ramirez** of BP focused on crude oil refining using biocatalysis and biotechnologies. She addressed achievements of biorefining and potential interaction of conventional refining and biorefining. There have been large investments made in crude oil biorefining over the last 20 years, but that has only reached the pilot-plant scale. Crude oil refining is complex, said Ramirez, as hydrocracking and hydrotreatment occur at very high temperatures and pressures. The products of crude oil refining include petroleum gases, naphtha, kerosene, gas oil (diesel oil), lubricating oil, fuel oil, and residue which are made up of a variety of molecules rather than a single molecule.

According to Ramirez, biocatalytic processes could be useful in crude oil refining because:

- they moderate conditions such as pressure and temperature;

- the chemistry is oxygen-based compared to hydrogen in hydrotreatment;
- the handling is facilitated by the conditions used;
- selectivity in biocatalysis involves a specific compound, while catalytic hydrotreatment involves a family of compounds;
- their application addresses improvements in product quality;
- they may minimize pollution and waste;
- they simplify the refining process by reducing separation and disposal stages; and
- they offer economic benefits.

Ramirez then highlighted some achievements in biorefining. A wide range of biocatalysts have been discovered from research at the cellular and subcellular level and have evolved through cloning and engineering of the microbial catalyst. Catalytic properties have been improved by broadening the selectivity of the biocatalyst. A more thermally stable catalyst has been patented and an attempt has been made to integrate those processes into refinery operations. Ramirez said that catalytic activity has particularly been improved for enzymes involved in desulfurization. A large effort in enzyme isolation and characterization has been made. Although some of the enzymes are known to contain metal clusters or metal sites, Ramirez noted that very little is known about their chemical nature and their catalytic role in the enzymatic action. She claims that scientists need to understand these issues in order to contribute to technology development.

Other biological processes have also been considered for improving refining. Ramirez sees that regulations on sulfur are becoming tougher and the supply of heavy oil is growing, leading to higher sulfur content in the feedstocks. Therefore, said Ramirez, producing the required cleaner products involves overcoming more difficult challenges. In conventional refining the hydrogen needs increase the operational costs, as a result of finding new chemistries for removing sulfur. Not much is known about the active site in the biological catalysts or the molecular mechanisms. Ramirez explained that the metabolic pathway of desulfurization is well established. The pathway links the intermediate metabolites of the reaction, but it is not known how one molecule is converted into another. Performance relationships that are well known in chemistry or in ordinary heterogeneous or homogeneous catalysis are not valid in the biocatalytic mechanisms.

Does it make sense to mimic the structural catalyst or to mimic how they work? Ramirez thinks that scientists need to understand the function rather than the structure of biocatalysts, and that scientists should investigate how biocatalysts work rather than what they are. It is important, said Ramirez, to address the selectivity issues and improve the performance of a biocatalyst when mimicking ordinary chemistry. She feels that stability should be addressed

because biocatalysts are not stable at the conditions that refineries normally operate and that catalysis should be as efficient as possible.

Ramirez expects that biorefining will bring new insights into refining, new chemistry, and new processes that are more energy efficient and emphasize of product quality. In the end collaboration will lead to greener solutions for refining.

## ACADEMIC PERSPECTIVE

**Daniel Nocera** of the Massachusetts Institute of Technology began his presentation by discussing a paper he wrote for the Proceedings of the National Academy of Sciences in 2006<sup>1</sup> in which he introduced a roadmap for chemistry's role in the energy problem. The rest of presentation focused on breaking the nearly linear dependence of energy use and carbon (i.e., replacing coal, gas, and oil). Nocera stated that the world is on an oil curve in terms of depending on carbon for primary-energy use. If coal is going to be used, posed Nocera, more efficient processes for mining, burning, and sequestering carbon should be developed. Population, GDP per capita, and energy intensity determine how much energy will be needed.

Nocera explained that the chemical equation for his research is oil = water + light. High-energy bonds, such as carbon-carbon, hydrogen-hydrogen, and oxygen-oxygen, are rearranged to produce a fuel. When they are burned, bonds are rearranged to produce energy. Nocera believes that the best crops to use for biomass conversion in terms of light energy storage are switchgrass, miscanthus, and cyanobacteria. Corn is the crop that is usually mentioned, said Nocera, because of the corn industry's lobbying effort and because conversion of starch to ethanol is well understood. Corn is an energy-intensive crop, requiring a large amount of energy to generate high-energy polymers in sugar and starch versus cellulose and lignin. Switchgrass and miscanthus have hardly any sugar or starch in them; they are made up of cellulose and lignin. Therefore, new microbes or thermochemical catalysts for lignin and cellulose conversion need to be discovered, said Nocera.

Nocera is concerned about the amount of carbon dioxide in the atmosphere, and he showed a public education video that he helped produce. He believes the carbon dioxide problem can be solved with water and light, which involves bond rearrangement. Therefore, said Nocera, the only types of energy that will work, from a renewable and sustainable perspective, are biomass, photochemical, and photovoltaic. He sees a problem with biomass in that it is also a food source, so biomass could be limited to a minor role in the energy future.

Nocera then discussed how photosynthesis demonstrates a bioinspired design. He suggested setting up a wireless current that is driven by the sun. A cathode, which produces

hydrogen, would be placed on one end and an anode on the other. Reduction would take place and the anode would drive water oxidation. The process ends up separating catalysis from capture and conversion.

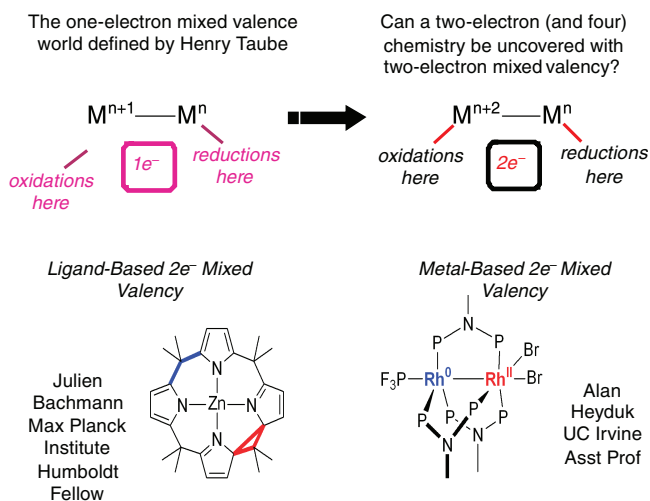
Nocera listed the main factors that will change for enacting solar energy:

- Cheap and efficient PVs;
- Replace noble metal catalysts (for fuel and solar cells) with inexpensive metals;
- New chemistry for water splitting.

He noted the need to manage electrons and protons, assemble water, and transfer atoms to make solar energy efficient with cheap catalysts. His team has developed several new techniques, such as proton-coupled electron transfer (which he noted as a human health issue). This technique is related to energy because it is how energy is stored in the biology realm. Nocera provided some examples of research being done in this area. One project involves inventing multielectron chemistry with mixed valency in which metals can be changed by two electrons using ligands (Figure 2.4).

The main conclusions from Nocera's presentation were:

- The need for energy is so enormous that conventional, long-discussed sources will not be enough.
  - Solar + water has the capacity to meet future energy needs.
- But large expanses of fundamental molecular science need to be discovered. There are many intriguing problems to study.



**FIGURE 2.4** Three projects demonstrating multielectron chemistry with mixed valency.

SOURCE: Presented by Daniel Nocera.

<sup>1</sup>Lewis, N. S. and D. G. Nocera. 2006. PNAS 103: 15729-15735.

— Renewable energy research is not an engineering problem. It has to be tackled as a basic science problem. Catalysis and many new modes of reactivity await discovery.

- Chemistry is the central science of energy because it involves light capture and conversion with materials and storage in bonds.

- The problem is too important to let our scientific egos get in the way. There needs to be an honest broker (i.e., objective group of scientists) who can recommend an honest representation of the strategic investment for energy.

Following Nocera's presentation, John Turner of the National Renewable Energy Laboratory said that the processes that Nocera discussed are missing something in the theory that would explain how to make the inorganic materials mimic what has been done with ruthenium and

platinum. Turner thinks there are too many combinations and a better directed approach is needed. Turner also suggested that they get theorists involved in the process to help understand synthesis and characterization. Nocera agreed with Turner's comment.

**John Sheats** of Rider University pointed out that along with the increasing need for energy, a population of nine billion people will need to be fed. He posed the question, "Can we use biomass for fuel and feed the world when we're not currently feeding the world?" Nocera responded with a simple "Yes," and mentioned that the food dilemma is why the problem of biomass conversion needs to move on to lignin and cellulose. Nocera stressed using other energy sources besides biomass. He explained that if the majority of the world's energy needs were addressed by using biomass, then there would indeed be a problem.

## 3

# Fundamental Aspects of Bioinspired Chemistry for Energy

Marcetta Darensbourg, Thomas Rauchfuss, Michael Wasielewski, and Charles Dismukes presented examples of the fundamental research being done at their institutions.

## HYDROGENASES AS INSPIRATION

**Marcetta Darensbourg** of Texas A&M University began by explaining the motivation for research on hydrogenases in the 1930s. Marjory Stephenson was the first person to discover hydrogenases in microorganisms that were responsible for the pollution in the River Ouse in Cambridge, United Kingdom. She looked at reactions, such as the fermentation of glucose, and concluded that there was an enzyme in the cells that produced hydrogen and enzymes that absorbed hydrogen in processes important to the production of methane. In one of Stephenson's papers she noted, "Bacterial coli has been shown to catalyze the oxidation of dihydrogen to two protons, releasing two electrons in a completely reversible way. The hydrogenase system is the most negative reversible oxidation reduction as yet described in living cells." Later, this activation was found to proceed from the heterolytic splitting of dihydrogen (i.e., to a proton and a hydride). Each decade following the initial discovery of hydrogenases brought tremendous advances, but in this century, Darensbourg noted another motivation for research: applying them to biotech challenges.

Darensbourg described how Fraser Armstrong (University of Oxford) and Antonio DeLacey (Universidad Autonoma de Madrid) are making enzyme electrodes in order to establish the hydrogen uptake and hydrogen production ability of the enzymes. Armstrong has calculated that on a graphite electrode, nickel-iron hydrogenase catalyzes hydrogen oxidation at a diffusion-controlled rate that matches the rate achieved by platinum. However, said Darensbourg, there are problems associated with the enzyme-electrode technology:

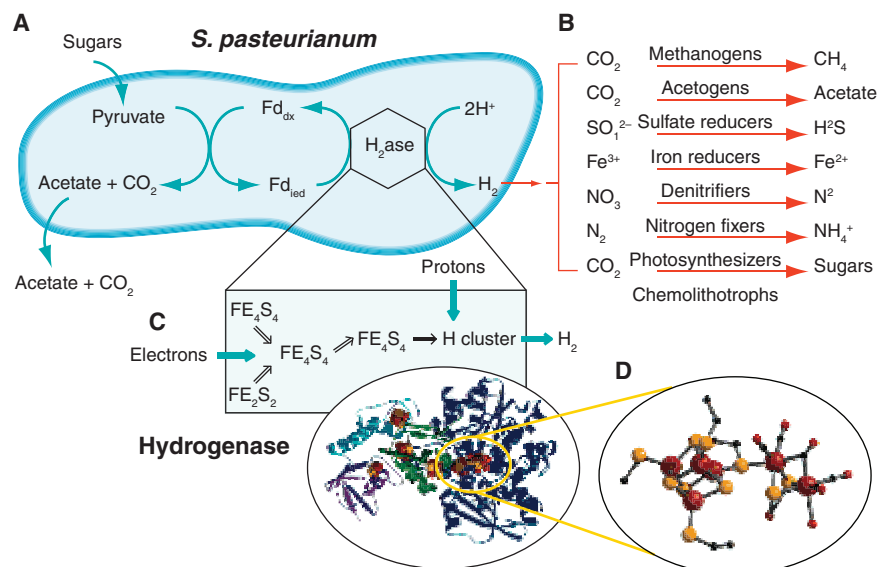
(1) the enzymes are derived from air-sensitive extremophiles; (2) while some can be tailored to be less air sensitive, most are of questionable robustness; and (3) they weigh a lot more than platinum. Hence, the bioinorganic chemistry approach to these problems involves preparation of small-molecule synthetic analogs that have the essence of the enzyme's metal-containing active site while reducing the amount of biomatter surrounding it. Darensbourg's research goals and those of others around the world substitute abiological ligands to engender the exact electronic environment of the metal that would allow it to have the same function it has in the complicated protein matrix. Ultimately they would like to attach them to carbon electrodes.

## Hydrogenase Structures and Functions

Darensbourg then described the structures and functions of the hydrogenases (Figure 3.1), pointing out the common factors of the active sites of two classes of iron-sulfur cluster containing hydrogenases (Figure 3.2), which are genetically distinct and evolved along different pathways, yet ended up at the same point in terms of function. She looked more closely at the all-iron hydrogenase, pointing out the iron-sulfur clusters that serve as a molecular wire into the hydrogen cluster that are a built-in electron-delivery system. She pointed out a second coordination sphere effect on the active site, which, if modified, will reduce the activity of that enzyme. With such complexities, the obvious question posed by Darensbourg was: "Will a small molecule modeled solely on the two-iron subsites be an electrocatalyst for hydrogen production or hydrogen uptake in oxidation?"

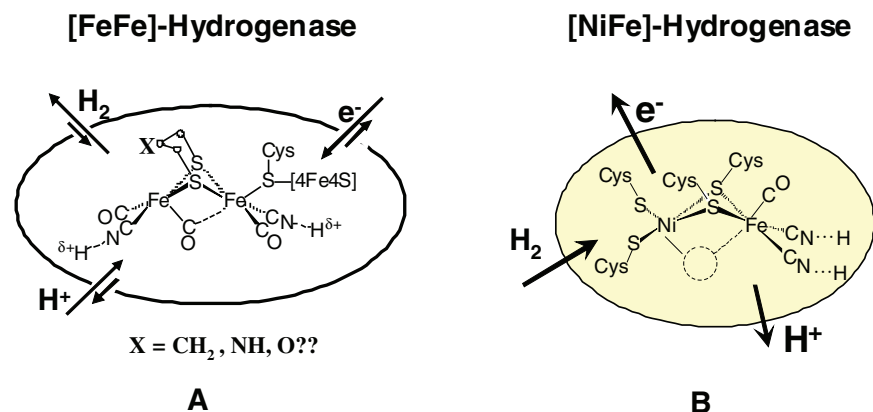
Darensbourg, Tom Rauchfuss, and Chris Picket saw a simple diiron organometallic molecule as an obvious mimic of the iron hydrogenase active site. Darensbourg said that this comparison was a good starting point for modeling





**FIGURE 3.1** Schematic of hydrogen metabolism and the hydrogenase active site. (A) The cell of *C. pasteurianum* whose metabolism involves the oxidation of sugars and evolution of hydrogen by the iron-only hydrogenase designated as a hexagon. (B) The range of organisms that use hydrogen as a reductant and use the nickel-iron uptake hydrogenase. (C) Schematic of the iron-only hydrogenase enzyme showing paths for electron and proton transfer converging at the H center. (D) Schematic of the H center showing the six-iron cluster with a two-iron subcluster bound to five CO or CN<sup>-</sup> ligands.

SOURCE: Adams, M.W.W. and E. I. Stiefel. 1998. Biological Hydrogen Production: Not So Elementary. *Science* 282(5395): 1842-1843.



**FIGURE 3.2** Examples of two of the main iron-sulfur cluster containing hydrogenase active sites.

SOURCE: Modified from presentation of Marcetta Darensbourg, Texas A&M University, based on crystal structures derived by (A) J.W. Peters and coworkers, 1998. X-ray crystal structure of the Fe-only hydrogenase from *Clostridium pasteurianum* to 1.8 Angstrom Resolution. *Science* 282(5395): 1853-1858; and (B) J.C. Fontecilla-Camps and coworkers, 1995. Crystal structure of the nickel-iron hydrogenase from *Desulfovibrio gigas*. *Nature* 373: 580-587.

studies in conjunction with vibrational spectroscopy of diatomic ligands. This could be used to match properties of the enzyme active site with the small molecule models. The diiron organometallic molecule has several attractive features, such as the flexibility associated with the iron dithiacyclohexane ring as it switches between chair-boat forms, flipping the bridge-head carbon in the process. This

feature can be monitored by nuclear magnetic resonance (NMR) spectroscopy. Darensbourg noted that additional flexibility is in the Fe(CO)<sub>3</sub> units on each end of the diiron complex, which shows intramolecular CO site exchange also detectable in variable temperature NMR experiments. As a result of studying the fundamental properties of the molecule, Darensbourg and others found that there are still

some key differences between the structures of the enzyme's active site and the synthetic model. She claimed the biggest difference is the orientation of the diiron sites, which are composed of sulfur-bridged square pyramids. In the synthetic analogue, these square pyramids are symmetrical with respect to each other; the apexes of the pyramids are pointed out and away. However, in the enzyme, one square pyramid is inverted or rotated with respect to the other. When that rotation occurs, said Darensbourg, it positions a carbon monoxide underneath the iron-iron vector, which is very important in preventing reactions that are dead ends for the catalytic cycle. Darensbourg and others found that the following tweaks to the molecular models are necessary to produce a more precise synthetic mimic:

- Multiple and asymmetric substitutions;
- Redox active ligand;
- A rotated structure that yields a bridging or semi-bridging CO ligand; and
- Access to a stable Fe(II)Fe(I) complex.

### Asymmetric Model Compounds

Darensbourg explained that early work found facile routes to asymmetric model compounds that demonstrated electrocatalytic hydrogen production in the presence of added aliquots of acetic acid. However, platinum is still a much better catalyst under the same conditions. Darensbourg then discussed how graduate student Tianbiao Liu explored derivatives of diiron carbonyl complexes with multiple CO ligand substitutions. Liu saw that in the cyclic voltamogram of an N-heterocyclic carbene(NHC)/trimethylphosphine complex there are reduction events at -2 volts, close to the solvent window. The oxidation, however, was fully reversible at -0.47 volts. As this oxidation wave is removed from everything else, Liu concluded that he might be able to isolate the oxidized product, and indeed he did. The oxidized product can be reduced back to the original compound, making it a fully reversible redox event, chemically and electrochemically. There was a reorientation of the NHC side of the compound, while the iron dicarbonyl phosphine side remained the same. This mixed-valent Fe(I)Fe(II) complex looked very much like the active site of the all-iron hydrogenase.

Darensbourg posed the question: Which is iron (I) and which is iron (II)? Mike Hall and Christine Thomas (Texas A&M University) are looking at this structure using density functional theory (DFT). The HOMO-1 and HOMO-2 are localized to the IMes NHC ligand. From the DFT study various parameters can be extracted, including unpaired spin density. Hall and Thomas found that the unpaired spin density lies primarily on the rotated iron, rather than the unrotated one, implying that the oxidation, the iron (II), is on the latter while the open-site iron is iron (I). The HOMO of the starting material is the iron-iron bond. Thomas has taken the iron(I)iron(I) precursor and twisted it to match the

geometry of the iron(II)iron(I)oxidized species, which is the same as adding an electron to the species. The HOMO of the reduced species in a rotated orientation has electron delocalization over the bridging carbonyl and a large amount of electron density at that open site. The significance of these rotated forms, explained Darensbourg, is that the HOMO is located on the accessible face of the iron and is poised to take up a second electron and a proton to make dihydrogen in the reduced form. In the oxidized form, the SOMO (singly occupied molecular orbital) is also on the open face, the accessible face, and is poised to give up an electron. If this configuration is maintained, there would be two iron (II)s and the species would be amenable to binding of H<sub>2</sub>. In other words, said Darensbourg, this is the inactive or resting form of the potential catalyst and it matches the resting form of the enzyme that was isolated and structurally characterized.

Darensbourg asked, "Does our molecule, with that seemingly open face, do anything? Will it bind dihydrogen or will it bind CO?" If we change this highly sterically hindered N-heterocyclic carbene ligand to the dimethyl N-heterocyclic carbene, we see CO binding and we see a stable carbonyl adduct. Other questions posed by Darensbourg included: "What are the radical properties of this molecule? Will it bind hydrogen atoms? Will intermolecular CO exchange occur rapidly?" She said that they are exploring the molecule's stability under carbon monoxide and then will look at CO exchange with added <sup>13</sup>C-labeled CO.

The key conclusions of Darensbourg's presentation were:

- The unusual "rotated" structure of the enzyme active site is achieved in a mixed-valent Fe(II)Fe(I) complex, which uses the unique orientation of a bulky NHC ligand to protect the open site on the rotated iron.
- The odd electron is on the open face of the rotated Fe(I).
- The 17-electron Fe(I) promotes CO exchange with exogenous <sup>13</sup>CO.
- This structure mimics the resting state of the [FeFe]hydrogenase active site. The enzyme holds this conformation in position throughout proton/electron coupling/decoupling reactions.
- What sort of synthetic matrix or solid support might restrict reverse rotation in such "rotated" structures?

### New Chemistry

**Thomas Rauchfuss**, University of Illinois at Urbana introduced his presentation by explaining that there is a lot of organometallic chemistry occurring in nature. In addition, he said the country's future is likely to be tied to synthetic gas, so there is a need for research on bioinspired syngas-like chemistry. Some of the key actors discovered so far include the aerobic CODH (CO dehydrogenase). He noted that hydrogenases are remarkable; they evolved independently

three times over 3 billion years and each time produced an iron carbonyl.

Rauchfuss' research team is interested in connecting  $H_2$  to iron to activate hydrogenation in fuel cells. There are only three crystal structures on the hydrogenase compounds, and they are extremely precious, he said. The structure of the CO-inhibited structure has been revised based on IR data.

He presented the design of the hydrogenases and pointed out that one of the major problems is that these systems are subject to dynamic equilibria. All of the substrates, electrons included, are transported in and out of the active site in a very specific way based on numerous studies.

Greg Kubas of Los Alamos National Laboratory has determined how hydrogen interacts with metals. The important part of his work is that hydrogen, a substrate that is redox inactive substrate and not Brønsted acidic, transforms upon complexation whereupon the coordinated  $H_2$  becomes acidic. The deprotonation of a metal dihydrogen complex generates oxidizable species and in this way,  $H_2$  is connected to electrons and heterolytic activation. Rauchfuss explained that Kubas' discovery has helped guide his team's effort to connect  $H_2$  binding to this redox-active iron metal.

Rauchfuss presented the catalytic cycle for the hydrogenases and pointed out two states that are most likely stopping points in the cycle (Figure 3.3). In his models, instead of using a complicated dithiolate, he is using a simple ethane dithiolate and replacing complicating cyanides and the iron-4 sulfur-4 cluster with phosphine ligands. It is a robust system, and very ordinary old Wilkinson-style ligands are used to support this complicated chemistry. After a lot of work, weak ligands can be installed on one iron and then subsequently replaced by a hydride. If the hydride is ter-

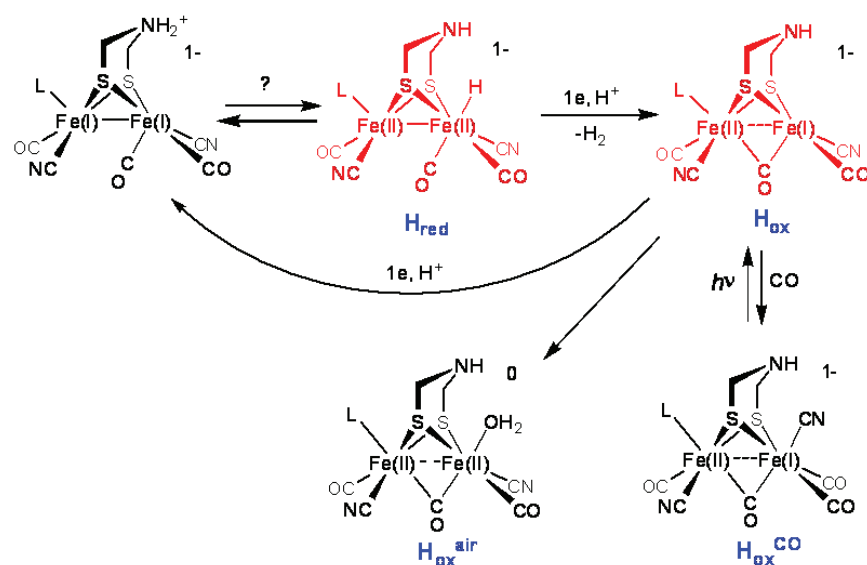
minal, it picks up protons and makes  $H_2$ . If it is left alone, it isomerizes and gives a bridging hydride, which does not form  $H_2$ . Rauchfuss sees this as an incredibly versatile and robust system.

Next, Rauchfuss explained how his team has used various chelating ligands to manipulate the symmetry of diiron models. The introduction of chelating agents changes the relative basicity and electronic asymmetry of the diiron models. His team has determined that electron-rich diiron complexes, made possible using chelating diphosphine ligands, are both redox active and Lewis basic (at the oxygen of the CO ligands). The redox chemistry of the diiron complex is sensitive to the presence of substrate and inhibitors used to determine what to bind to the extra position. Rauchfuss's team has examined a one-electron oxidized diiron model and is now wondering what happens if they doubly oxidize it.

The preparation of models for the  $H_{ox}$  state of the hydrogenase is an important breakthrough, noted Rauchfuss, and his group would never have considered this target without the guidance provided by structural biology. He also showed some of the other types of reactivity for the mixed-valence diiron complex and explained that the power of synthetic organometallic chemistry is contributing new concepts in hydrogen-activation and hydrogen-relevant chemistry.

### Noninnocent Ligands

Rauchfuss's team is working on noninnocent ligands, a family of ligands in which the oxidation state is unclear. A quinone is a typical noninnocent ligand that has not been used very much in hydrogen activation. Using such non-



**FIGURE 3.3** Catalytic cycle for FeFe-hydrogenases, with two most likely stopping points in the cycle highlighted in red.  
 SOURCE: Presentation of Thomas Rauchfuss, University of Illinois, Urbana-Champaign.

innocent ligands, the team is working on simulating the role of the iron-4,  $S_4$  cluster in the hydrogenases.

The team is trying to address the following questions: What happens when you put this system on a metal that might activate hydrogen? Can you use this design to encourage hydrogen activation? Rauchfuss thinks the results look promising. The ligand is active and it binds to virtually any substrate provided. If a base and hydrogen are provided to these complexes, the hydrogen is oxidized to protons. This is a system in which a metal that is otherwise uninteresting is “turned on” due to a ligand-based redox.

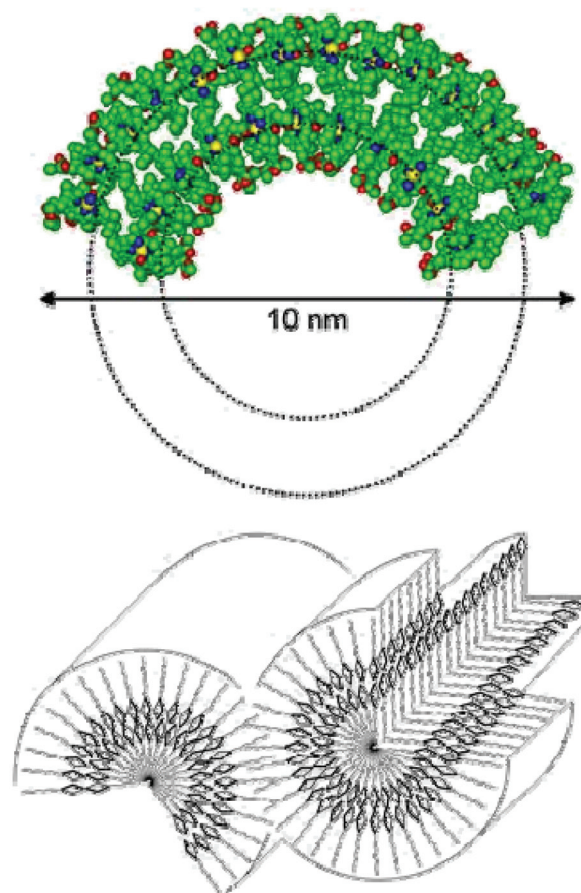
The challenging part of the fuel cell is  $O_2$  reduction. Rauchfuss’s team is interested in whether bringing an organometallic perspective to that type of reactivity. The team is wondering whether the old reaction of  $O_2$  plus  $H_2$  will work. Part of the problem, explained Rauchfuss, is that most compounds used to hydrogenate oxygen in a potential fuel cell application would produce hydroxides. A new family of hydrogen activating species is coming online in the near future. There may be a role for heterolytic activators of hydrogen in oxygen reduction for fuel cell development. Progress with these activators was illustrated with an experiment conducted in an NMR tube, a Knallgas reaction. Nickel-iron hydrogenases carry out and effect a similar  $H_2 + O_2$  reaction to provide energy for certain bacteria.

Rauchfuss concluded by restating his main point: Synthesis enables translation of mechanistic insights into catalysis and is a critical component of the overall bioinspired effort. Even though redox chemistry and hydrogen seem quite old, the field is wide open for new discoveries.

## ARTIFICIAL PHOTOSYNTHETIC SYSTEMS FOR SOLAR ENERGY CONVERSION

At Northwestern University **Michael Wasielewski** and his team are trying to understand various biological processes relevant to energy, especially photosynthesis. They hope to achieve different protein environments and different juxtapositions of the cofactors relative to one another to elicit a specific function of bioinspired and biomimetic systems. This is critical, said Wasielewski, since society depends heavily on frontline synthesis.

In a biomimetic study being done by his team, the peripheral antenna complex from green-sulfur bacteria was investigated (Figure 3.4). The bacteria are unique because chlorophyll is associated with protein. The metal ligand bonds to protein, which bonds the chlorophylls to the protein. The particular antenna complex that he presented is unique because it relies on chlorophyll-chlorophyll interactions to produce a micellar structure. Wasielewski’s team has been able to use the ability of chlorophyll to glom onto itself to study some of the issues pertaining to energy transfer. Magnesium requires five ligands, so the fifth ligand can be one of the oxygen atoms of a corresponding nearby chlorophyll, such as the carbonyl group or a bridging ligand. In



**FIGURE 3.4** Light-harvesting peripheral antenna complex from green-sulfur bacteria consisting of self-assembled arrays of chlorophyll molecules.

SOURCE: A. R. Holzwarth, Max Planck Institute.

each case chlorophyll’s basic asymmetry gives one transition dipole moment, which is oriented in a particular direction. The coupling of the transition dipole moments are critical to the function of chlorophyll in spectral forms and the energy transfer properties gleaned from them.

Wasielewski stressed the importance of avoiding groups in the building block that could interfere with those positions. His team developed a new functionalization strategy for the 20 positions of chlorophyll so that there is a hook to attach other species and to use without getting in the way of self-assembly points of interest.

Wasielewski then focused on a particular ring structure found in antenna proteins to see how a system could be developed based on chlorophyll that mimics some of these features. It turns out that the spectral shift does not explain anything. He said that there needs to be a structural tool to present specific information. The Advanced Photon Source, the brightest X-ray source in the country, at Argonne National Laboratory, is currently being used for this purpose.



Wasielewski is also working on determining the structure of a four-fold symmetric cyclic ligamer that is forming a structure spontaneously in solution. His team is looking at spectroscopy to excite the system and identify any energy transfer and is putting two excitations in the molecule to study energy transfer. The result of the four fold symmetric system is that energy transfer occurs incredibly fast, at about a picosecond. This demonstrates that energy transfer in the self-assembled system is faster than most porphyrin systems involving covalent linkages and it is almost as fast as some of the quickest natural systems. Use of robust components in bioinspired systems is one that has become a major theme in Wasielewski's group.

The team is now interested in electron transfer in a stacked, noncovalently linked system, with an electron photochemically pumped in. If four of these molecules are placed around a porphyrin, explained Wasielewski, the system self-assembles into a large aggregate and because of the side groups in the system, an interlead aggregate results where every other layer is missing a porphyrin. Synthesis of the building block occurs, leading to a new type of self assembly. Side groups were eliminated and some long-tail end groups were substituted to aid solubility.

Given a differential recombination of charge when an ion pair is formed and the recombination rates are different, the direction of charge transport can be controlled by choosing which direction the electron enters. This is called a chlorophyll mimic. It has the same oxidation potential of chlorophyll and absorbs in the same place that chlorophyll does.

Wasielewski noted the importance of compartmentalization in generating hydrogen and oxygen by splitting water. He discussed a paper that his team recently published<sup>1</sup> describing how a specifically tailored perylene diimide-type system can build a nanotube. Wasielewski concluded that this kind of approach shows what the next step of bioinspiration will be in developing systems for artificial photosynthesis.

## WATER SPLITTING BY BIOINSPIRED CATALYSTS

**Charles Dismukes** of Princeton University focused his presentation on one reaction that splits water to create oxygen. He highlighted new developments in bioinspired catalysis that mimic the active site of the water-splitting enzyme of green plants and other oxygenic phototrophs. Drivers for this research include economics, gasoline prices, political issues, and the environment. Dismukes said, "I like to think that we have a golden opportunity right now because of the motivation that many of the young people are experiencing from these forces."

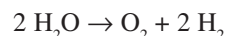
The availability of platinum is a limitation to hydrogen production at the anode and for oxygen reduction at the cathode of fuel cells. Unlike the anode reaction, explained

Dismukes, the use of platinum as the electrode material for oxidizing water requires a large overpotential to drive the reaction and thus is not ideal. Nonprecious metal catalysts are needed for water oxidation and integration into cells that use light in terms of the overall reaction.

### Photosystem II Water-Oxidizing Complex

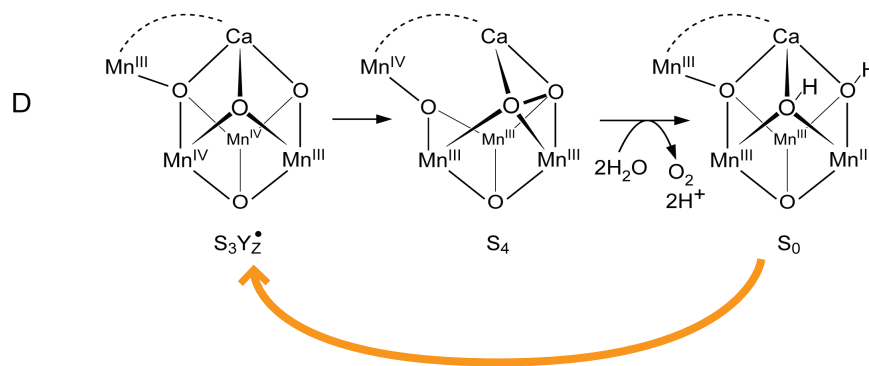
Dismukes explained how photosynthesis splits water, produces oxygen, and extracts electrons and protons to undergo fixation of carbon dioxide. The enzyme that carries out the water oxidation process is called photosystem II water-oxidizing complex (WOC). There have been developments in the last three years on the crystallography of proteins involved in the process. Prior to that, chemistry and spectroscopy have provided much data about functions of the enzyme. Three crystal structures has been reported for this enzyme, which has evolved for about 3 billion years to achieve its current catalytic efficiency. Dismukes said that there is only one example of this evolved enzyme, which is found in all terrestrial plants, green and red algae, and bacteria. There is no variation of this blueprint across the entire range of oxygenic phototrophs.

Dismukes described how coworker Gennady Ananyev and students in Ananyev's group are characterizing oxygenic phototrophs that can operate at pH 0 up to pH 12 in every redox environment and many toxic metal environments. The emergence of a single enzymatic blueprint for catalyzing water oxidation chemistry is a critical clue that Dismukes says should not be overlooked in the design of engineered catalysts. These enzymes constitute nature's optimal design achieved through combinatorial biosynthesis. The bioinspired approach relies on adopting nature's blueprint for catalyzing the lowest-energy five-bond rearrangement necessary for the water splitting reaction:



Working with graduate students Jyotishman Dasgupta and Rogier Van Willigen, Dismukes described their proposed mechanism for how the native WOC enzyme catalyzes oxygen production from water (Figure 3.5). After accumulation of four holes and release of protons into solution, the highest oxidation state of the cluster is reached. The oxidation states represented are not unequivocally established by any of the spectroscopy thus far. A chemist looking at that structure will think it is intrinsically unstable based on the structure of the bridging tetrahedral oxygen atom. The oxygen prefers to rearrange into a coplanar arrangement with three manganese atoms. In other words, said Dismukes, the oxygen will sacrifice a weak single bond to a calcium ion in favor of forming a multiple bond to three manganese atoms. In this view of the mechanism, a tetrahedral oxygen atom would go coplanar, cleaving the bond and allowing the calcium to move over to bind to a peroxide intermediate that

<sup>1</sup>Sinks, Rybtchinski, Jones, Goshe, Zuo, Tiede, Li, and Wasielewski, 2005. *Chem Mater* 17: 6295-6303.



**FIGURE 3.5** One of the postulated pathways for the  $\text{O}_2$  release step of the WOC. The naturally occurring WOC of photosystem II is able to efficiently photooxidize water in a sustainable manner using visible light according to the reaction:  $2 \text{H}_2\text{O} \rightarrow \text{O}_2 + 4 \text{H}^+ + 4 \text{e}^-$ .  
 SOURCE: Presented by Charles Dismukes.

forms between what were formerly two oxo bridges. This is the proposed slowest step and represents the activation barrier to forming the highest energy intermediate of the reaction. Subsequent release of  $\text{O}_2$  by a further two-electron transfer reaction from the peroxide to manganese is thermodynamically favored and occurs spontaneously.

### Manganese-oxo Cubane

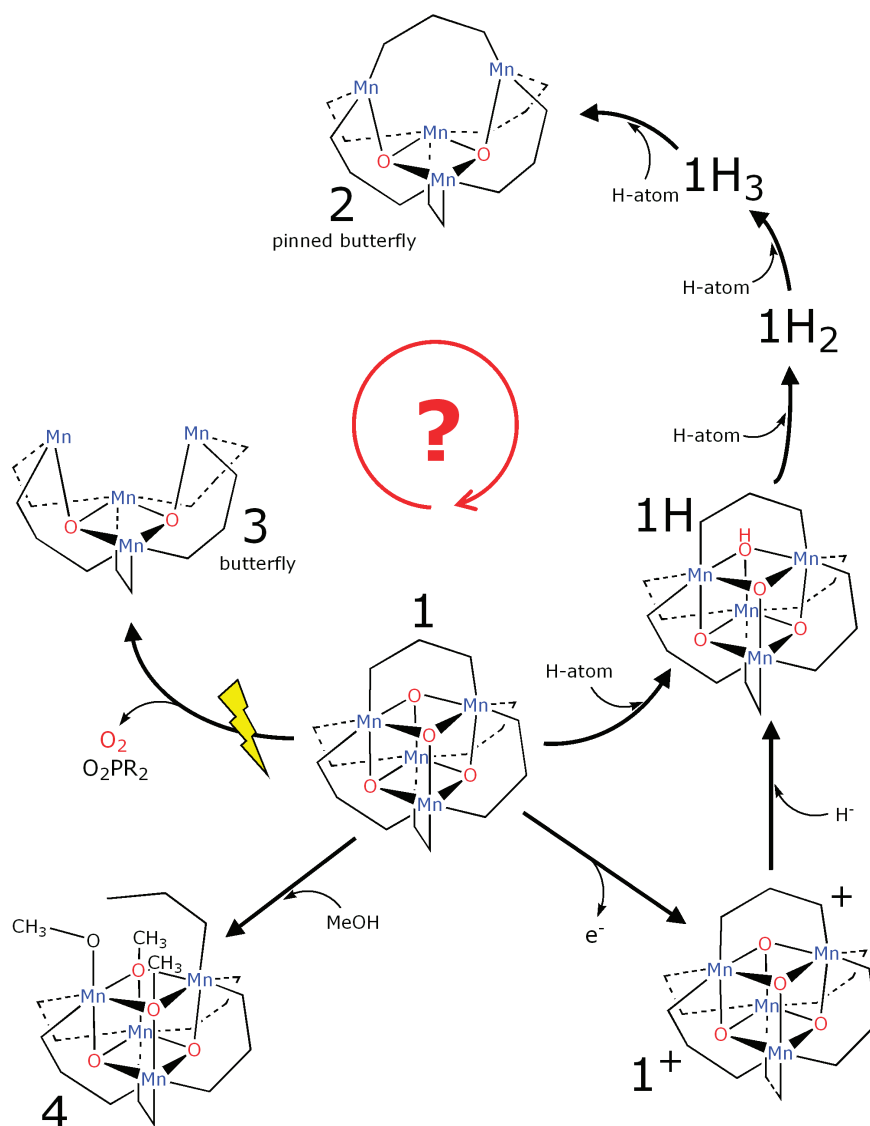
Dismukes showed a manganese-oxo cluster sharing structural features with the WOC, which exhibits  $\text{O}_2$  formation by an analogous pathway. These manganese-oxo cubane molecules possess the  $\text{Mn}_4\text{O}_4$  core type and were unknown core types in inorganic coordination complexes until first synthesized by graduate student Wolfgang Ruettinger (complex 1 in Figure 3.6).

Dismukes discussed the oxygen-evolving chemistry in the gas phase (Figure 3.6). When the molecules are vaporized into the gas phase using UV-visible light, most of them release oxygen (60-100 percent depending on choice of phosphinate derivative). This is a laser desorption ionization-mass spectrometry experiment (LDI-MS). In the gas phase they can either thermalize to form the unmodified cubane in its ground state or dissociate by releasing a phosphinate ligand and an oxygen molecule. Importantly, said Dismukes, the only other product is the intact “butterfly” compound 3,  $\text{L}_5\text{Mn}_4\text{O}_4^+$  (Figure 3.6), as was shown in the positive-ion LDI-MS. Dismukes found that removal of a single phosphinate is required to achieve the flexibility needed to form and release  $\text{O}_2$  in the gas phase. Calculations by Princeton colleagues Filippo DeAngelis and Roberto Car showed that the activation barrier for  $\text{O}_2$  release from the resulting  $\text{L}_5\text{Mn}_4\text{O}_4^+$  intermediate is much smaller at 23 kcal/mol. This is called the jack-in-the-box mechanism for oxygen release. When the photolysis is carried out in condensed phases, either solid state or in organic solvents that dissolve the cubane, there is no  $\text{O}_2$  release and

no net photoreaction occurs. In the condensed phase the barrier to  $\text{O}_2$  release is too large to surmount rapidly such that the phosphinate does not dissociate or rebinds so fast that it prevents the  $\text{O}_2$  from forming. Thus, if an open-face cubane with a lower barrier to  $\text{O}_2$  release could be prepared, the system could in principle be used in a catalytic cycle to convert water into  $\text{O}_2 + 4 \text{H}^+$  and  $4 \text{e}^-$ . All of the gas phase work has been published.

Dismukes spoke about his team’s recent efforts with Australian collaborators from Monash University (Robin Brimblecombe and Leone Spiccia) and Commonwealth Scientific and Industrial Research Organisation (Gerhard Swiegers) to examine methods to achieve a catalytic water oxidation cycle by doping cationic cubanes compound  $1^+$  (Figure 3.6) in the aqueous channels of proton-conducting membranes like Nafion®. Nafion is a fluorinated polymer with ionizable sulfonic acid head groups that remain hydrated in water and form aqueous channels that are about 20 nm in diameter. The channels are permeable to cations but not anions since they are “lined” with sulfonate groups whose charge is balanced by mobile cations ( $\text{H}^+$  or  $\text{Na}^+$ ). Nafion is readily deposited as a thin layer upon electrode surfaces. The cationic cubane species was doped in thin Nafion films by ion exchange in acetonitrile. Replacement of the  $\text{CH}_3\text{CN}$  solvent by water traps the hydrophobic cubane in the channels of the film. Voltammetry detected the redox transition  $1 \leftrightarrow 1^+$ , thereby unequivocally confirming the presence of the cubane in the Nafion film. It also established that direct electron transfer occurred readily between the immobilized cubane and the underlying electrode.

When polarized at a potential of 1 V (vs Ag/AgCl), the resulting electrode assembly generates a transient dark current corresponding to the complete oxidation of  $1/1^+$ . Subsequent illumination by UV-visible light generates a large increase in this current, which systematically and reproducibly tracks with the duration of the light interval as it is switched on and off. Gas bubbles form at the



**FIGURE 3.6** Redox reactions and photochemistry of  $\text{Mn}_4\text{O}_4(\text{Ph}_2\text{PO}_2)_6$ .  
 SOURCE: Presented by Charles Dismukes.

photoanode, and analysis by GC-MS confirmed this to arise from isotopically enriched  $^{36}\text{O}_2$  (produced using  $^{18}\text{O}$  water). Several experiments illustrated the wavelength dependence, the pH dependence, and the solvent dependence, all of which confirm that water is the oxidizing reactant for  $\text{O}_2$  production. The electrochemical conversion of charge was shown to match the volumetric yield of  $\text{O}_2$ . Dismukes thinks these results hold promise to an exciting new approach for water oxidation based on the principles inspired by nature. This work has been submitted for publication.

At the end of his presentation Dismukes talked about the next steps for his research. His group does not want to use UV light to activate the system, but they understand that the

light is necessary to knock off the ligand. As they investigate the possibility of using catalysts that can accept weaker-field phosphinate ligands, they can replace the stronger phosphinates with weaker-binding phosphinates or possibly other ligands. His group also thinks they can make some heterocubanes by fusing two classes of metal dimers. Dismukes said that it would be helpful to try to put alkaline earth ions in there. They plan to look at other proton exchange membranes on the market. He also said that some conducting polymers would be very helpful. They think they are processing only the first 50 nanometers or so the catalyst, so they want to include polymers that would allow them to be transferred to a much farther distance.

## DISCUSSION

During the discussion period, some participants were skeptical of Charles Dismukes's research. **Thomas Moore** of Arizona State University asked Dismukes whether he could show quantitatively that a molecule of cubane really turns over multiple times. Dismukes said that the electrochemistry data shows that after a cycle of the system, electrochemical potentials can be seen for the  $2, 2^+$  couple. His team is trying to take the material that has been cycled and do X-ray spectroscopy on it. They have also looked at photodegradation products like manganese dioxide. **Gary Brudvig** of Yale University pointed out that Dismukes claims hundreds of thousands of turnovers, which is much higher than a natural system. Dismukes backed up his research and explained that the molecules produced oxygen in the gas phase with very high quantum yield and with no other photochemistry.

Daniel Nocera of MIT raised an important issue about how scientists approach the public with regard to the details of their research. Nocera warned the group that they can lose the public's confidence if they are overenthusiastic and do not back up their research results, stating that, "The public

won't have patience for our excitement if it's wrong. So we should hash this out among ourselves and then present only to the best of our ability what we know is right." Thomas Rauchfuss of the University of Illinois agreed with Nocera's point and said that a good example is the overenthusiasm for hydrogen. He thinks people are under the impression that when hydrogen is produced by electrolysis a major problem has been solved. However, Rauchfuss feels the bigger barrier is integration of hydrogen into the energy infrastructure. He also explained how ethics comes into play when scientists want to promote their work to the public in order to receive more funding. On the other hand, Judy Raper of the National Science Foundation said that it is important to get students interested in engineering and science, so there has to be a balance between ethics and informing the public about the research being done.

**Sharon Haynie** closed the fundamental aspects session by pointing out the promise and perils of the bioinspired research. Haynie thinks there is promise because the public understands the current energy crisis; however, overpromising the research can lead to peril by disillusioning and alienating the public.





## 4

# Robust Implementation of Bioinspired Chemistry for Energy

During this session of the workshop, Thomas Moore, G. Tayhas Palmore, and Mark Emptage presented examples of how bioinspired chemistry for energy is being implemented within their organizations. These projects utilize some of the key fundamentals described in Chapter 3 to present the big picture of how bioinspired chemistry can improve the energy field.

### MIMICKING BIOLOGICAL ENERGY TRANSDUCTION

**Thomas Moore** of Arizona State University began by discussing how nature has adapted for 3.4 billion years through fierce evolutionary competition. He said that researchers need to follow nature's example, but accept the fact that in meeting human energy needs there may be ways to improve on nature. He defined the purpose of the workshop as a way to explore how to improve the natural process of photosynthesis and incorporate the kinetically and thermodynamically successful features in human-engineered constructs.

Moore compared the technological branch of solar energy conversion, essentially photovoltaics, with the biological branch. He explained how a standard fuel cell that operates on oxygen and hydrogen produces water and electromotive force. A typical human-engineered fuel cell operates at 50-60 percent power conversion efficiency and uses platinum or other noble metals as catalysts.

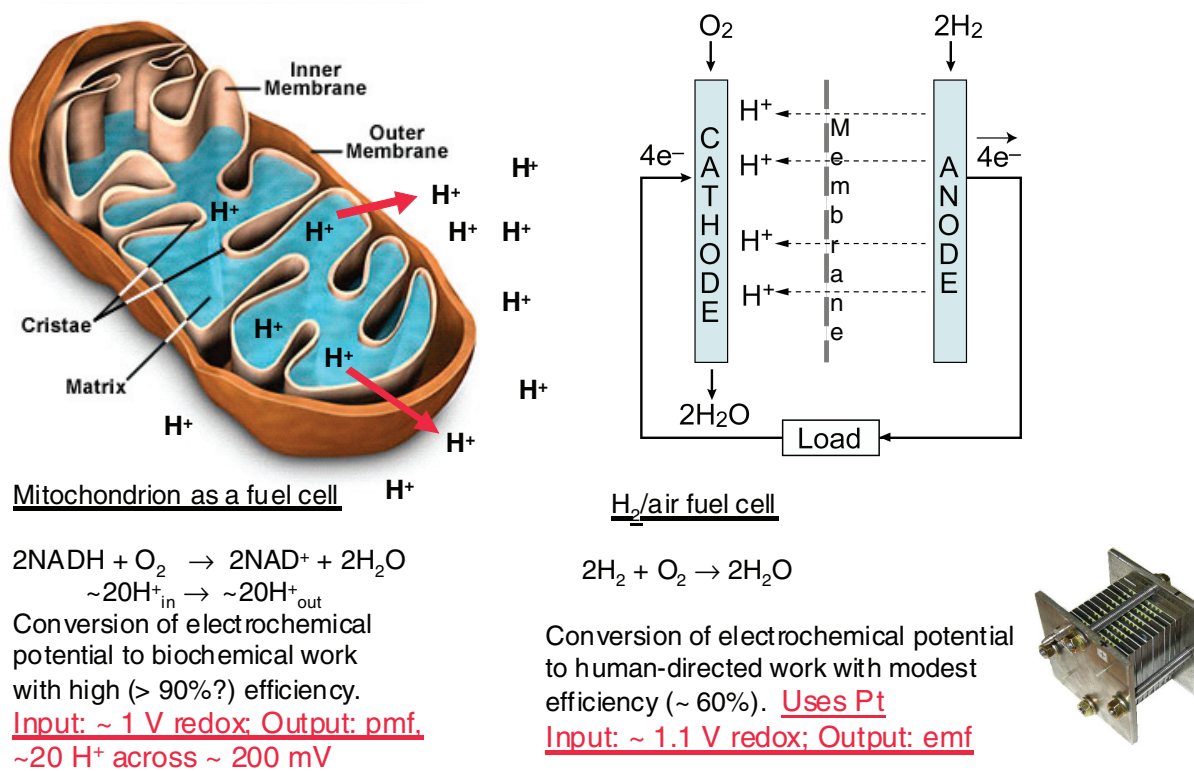
Moore then explained how mitochondria are biological fuel cells. The oxygen reduction taking place in a mitochondrion is exactly the same as in a standard fuel cell. Using several enzymes and only earth-abundant elements, the mitochondrion converts electrochemical potential to biochemical work with efficiency greater than 90 percent. This is a steady-state process in which protons are pumped across the membrane to maintain its electrical potential. If

the membrane potential drops by a factor of two, the cell dies. The high efficiency of energy transduction by mitochondria is the fundamental difference between standard fuel cells and mitochondria (Figure 4.1).

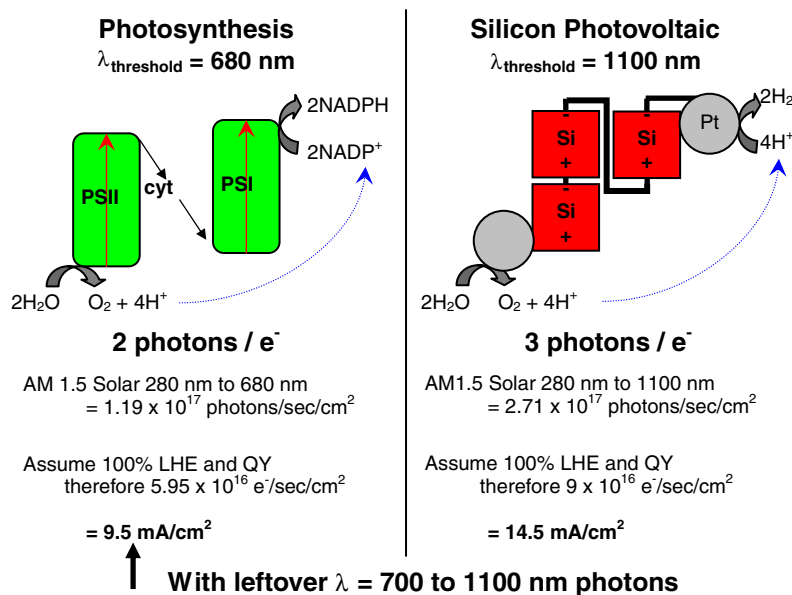
Moore talked about the opportunity to produce electricity with photovoltaics, but noted that a really important advance would be to use sustainably produced electricity to produce fuels for the transportation sector. Nature has the catalysts that direct reactions such as the reduction of  $\text{CO}_2$  to reduced, energy-rich carbon compounds. These catalysts operate at room temperature and yield essentially pure products. The problem is that these natural catalysts do not "recognize" electromotive force and cannot use it efficiently to drive synthetic reactions. The research challenge is to focus on effectively "wiring" enzymes into sources of electromotive force. He said that discovery is a key to achieving sustainable energy production and use. Arizona State University, for example, has a large metagenomics program in which researchers travel to various locations looking for microorganisms with catalysts that can carry out useful reactions.

Moore also compared water splitting by photosynthetic systems with a human engineered system consisting of three PV cells operating in series driving a commercially available electrolyzer (Figure 4.2). Series operation is necessary for Si-based PV cells to provide the voltage necessary to oxidize water and reduce protons to hydrogen in the electrolyzer. He pointed out that photosynthesis uses two photons per electron and has a threshold for absorption of light at about 700 nm. The PV cells need three photons per electron but, because their threshold is about 1100 nm, which means they gather about twice as many of the available photons, they are probably more efficient at water oxidation than photosynthesis.

Moore highlighted several projects at Arizona State University that are using biological and bioinspired chemistry for energy discoveries.



**FIGURE 4.1** Comparison of mitochondria and engineered fuel cells.  
 SOURCE: Presented by Thomas Moore, Arizona State University.



**FIGURE 4.2** Comparison of photosynthesis and a silicon-based photovoltaic system.  
 SOURCE: Presented by Thomas Moore, Arizona State University.

**Biodiesel to Fuel a Large Power Plant.** Researchers at ASU's Center for Bioenergy and Photosynthesis have calculated that a  $25 \times 25$  km field of bioreactors using cyanobacteria to fix carbon could uptake all of the carbon dioxide produced by a 1.6 GW power plant and subsequently provide the biomass as lipid to fuel the power plant. The parameters necessary to achieve this goal are a seven percent power conversion efficiency for photosynthesis, 40 percent conversion efficiency of biomass to fuel, 50 percent conversion efficiency of fuel to electricity, and 80 percent conversion efficiency of land area covered by the bioreactors. This system would then be carbon neutral in operation and produce about 1.6 GW of electrical power. The key to making this feasible is to achieve a seven percent power conversion efficiency for cyanobacteria. Moore noted that the area required to produce a specified amount of energy scales directly with the energy conversion efficiency of the system or device.

**Tubes in the Desert.** This project offers one approach to the design of bioreactors to produce biodiesel using the photosynthetic capabilities of microalgae or cyanobacteria. Solar energy conversion by photosynthetic organisms offers the almost inestimable advantage of self assembly, self replication and self repair of the key photoconverter. Cyanobacteria in bioreactors do not require arable land, which, Moore says, avoids the conflict of using agricultural land for energy production. The bacteria grows quickly year-round with a doubling time of 0.5-1.0 day. The reactors do not use a large amount of water, which is good for dry locations, such as Arizona. There is a high output of biomass: The practical range is 40-100 tons/ha/yr dry biomass and the optimal level is 500 tons/ha/yr. The output can be a high-value liquid fuel created with genetic and engineering controls. The process is not cellulosic or lignocellulosic, explained Moore.

**Hydrogenase on a Carbon Electrode.** Michael Graetzel designed a system that permits nanoparticulate material to absorb light using a dye. After it absorbs the light, the dye injects electrons into a conduction band. This creates electromotive force through an interface between a molecular system and a semiconductor. This experiment involved a Graetzel-type photo anode being sensitized by a porphyrin that upon excitation puts an electron into a wire that connects to a cathode. If the cathodic reaction is positive and there is a good catalyst, Moore explained that electromotive forces will be produced. But if the cathodic reaction is negative in electrochemical potential, such as proton reduction, energy-rich fuel is produced. After the electron injection, a radical cation of the dye is left. The cation then oxidizes a coenzyme, NADH, for which there are many different dehydrogenase enzymes that can oxidize many different bioorganic materials and reduce the NAD. NAD is thus a mediator or carrier of electrons between the bioorganic material and the photoanode. This type of electrochemical cell is nonregenerative,

providing the opportunity to produce reduced material. By using a platinum carbon cathode, hydrogen can be produced. Essentially, every two electrons produce one hydrogen from this process. In collaboration with a group at the National Renewable Energy Laboratory (NREL), scientists at Arizona State University have been putting hydrogenase enzymes on a carbon electrode to successfully produce hydrogen. Hydrogenase enzymes use only iron and nickel metals to carry out the catalytic process.

**Failed Water Oxidation Experiment.** Although direct water oxidation using an artificial photosynthetic device is not possible because the necessary catalyst does not yet exist, Moore is developing an approach to "push the envelope". His group is working to create a hybrid system that would use a naturally occurring photosystem II to oxidize water. Moore explained that the anticipated electron flow would be from illuminated PS II particles, oxidizing water, to the photoanode, where the process described above would produce hydrogen. Thus two photons would be used to move an electron from the redox level of water to the level of hydrogen—much in the same way that natural photosynthesis uses two photons to move an electron over roughly the same redox span. The output of photosystem II is a reduced quinone, a quinol. The quinols carrying the electrons from water would then be the input into the artificial system to produce hydrogen. Moore noted that the aim was to create a hybrid system to explore ways to couple two photosystems together and to investigate the thermodynamic and kinetic constraints involved. Unfortunately, this experiment has not worked to date.

Moore explained that the experiment failed because using the quinols as electron donors to the photoanode recombination limited the output potential to values that were not negative enough to reduce protons to hydrogen. When NADH is the electron donor, photo currents for hydrogen appear. When NADH is oxidized, a radical cation with a  $pK_a$  of -4 remains. This cation immediately drops the proton off, generating a species that donates a second electron. There is no recombination reaction and no recombination current from the mediator to the anode with that mediator. When a quinone mediator is used, the first electron is removed from the quinone and the radical species formed, and various semiquinones are in the electrochemical region where recombination reactions from the electrode can occur. The rate of this recombination limits the potential the cathode can reach. Moore talked about trying to use an electrode with a blocking layer to solve the problem. He concluded that the experiment raised some important questions about efficiency, redox span, and the limitations that must be overcome in wiring enzymes to electrical circuits. While nature obviously "got it right" for nature's purposes, there is room for improvement when using bioinspired processes to meet human energy needs.

## BIOFUEL CELLS

**G. Tayhas Palmore** of Brown University presented a diagram of the four components of energy conversion: biomimetics, purified or engineered enzymes, synthetic biology, and bacterial isolates. Palmore gave a brief tutorial on how fuel cells work (Figure 4.3). She explained how they convert chemical energy into electrical energy by separating the oxidation and reduction reactions into two separate chambers using a membrane. The anode is the electrode where hydrogen is oxidized to protons. The oxidation of hydrogen releases electrons drives an electrical load, which is coupled with the movement of ions through the membrane that drives the reduction of oxygen to water. For a hydrogen-oxygen fuel cell, the open circuit voltage is 1.2 volts. The three-phase interface between a catalyst breaks the bonds. A current collector then takes the electrons that are released from those bonds away from the active site. Finally, said Palmore, an ion conductor moves the protons or ions released away from the catalytic site to repeat the process.

Palmore also explained that the biomimetic approach uses inspiration from biology to develop new chemistry to perform catalysis. Palmore focused on using biology to do the energy conversion, both in the free form as purified enzyme extract and where new organisms have been isolated and coupled with electrode surfaces (Figure 4.4).

According to Palmore, the following parameters are important for both bio- and conventional fuel cells:

- Fuels, such as methanol, ethanol, glucose, and higher-level organics, can also be considered since they all have potentials similar to hydrogen. The fuel will depend on

what is used in the anode and what is used in the cathode, which is oxygen.

- The current density is also important and depends on the rate of catalysis and the movement of ions across the membrane.
- It is important to consider pH, temperature, and pressure since conventional fuel cells use catalysts that function at very low pH and high temperatures.

Palmore continued her talk with some examples of research that has been done in the field.

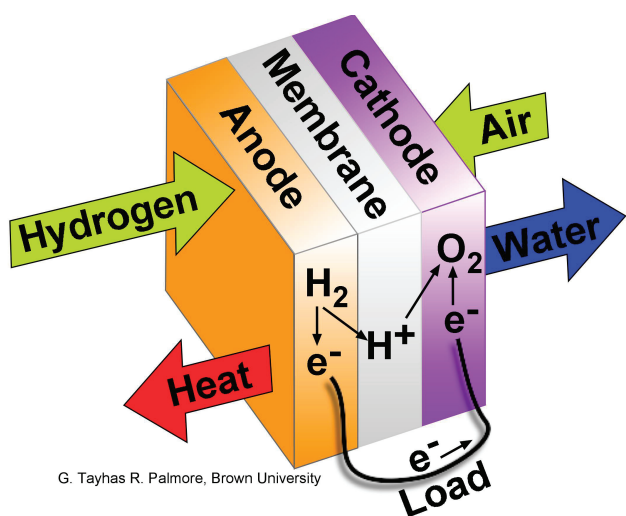
### *Itamar Willner and Eugenie Katz's Glucose Fuel.*

Willner and Katz (Hebrew University of Jerusalem) used an enzyme-based biofuel cell that had direct contact (i.e., tethered to an electrode) to produce glucose as a fuel.<sup>1</sup> The experiment showed the power of chemical control in organizing the assembly on the surface. Willner and Katz took advantage of modified thiol-gold chemistry, a PQQ mediator with the thiol, and added a reactive carboxylic acid that could be reacted with the FAD cofactor enzyme. Using a cathode reaction, they also demonstrated a truncated peroxidase that was tethered to the surface. They demonstrated that open-circuit voltage could reach approximately 140 microamps per centimeter squared. The maximum power was at about 32 microwatts. The voltage was low because peroxide was used as the oxidant instead of oxygen.

**Adam Heller's Glucose Fuel.** Another example of enzyme-based glucose oxidation was done by Heller's group (University of Texas at Austin).<sup>2</sup> They worked with redox-active polymers, which are molecular wires. Heller's team used the osmium-bisbipyridine complexes and tuned them with their ligands to adjust the potential relative to an anodic fuel like glucose or a cathodic fuel like oxygen. The complexes were then immobilized with the enzymes to catalyze the conversion of glucose to gluconolactone and oxygen to water. The system demonstrated the following:

- It is a membrane system, physically separating the anodic and cathodic reactions.
- It survived about seven days before the current began to diminish.

Palmore pointed out how difficult it is to reduce oxygen to water, and explained that it can be done using a number of enzymes in the copper oxidase family. She has used laccase because it is a monomeric protein but is unlike dehydrogenases that depend on a cofactor and a binding site. Laccase has a redox center of four copper ions that are reduced from

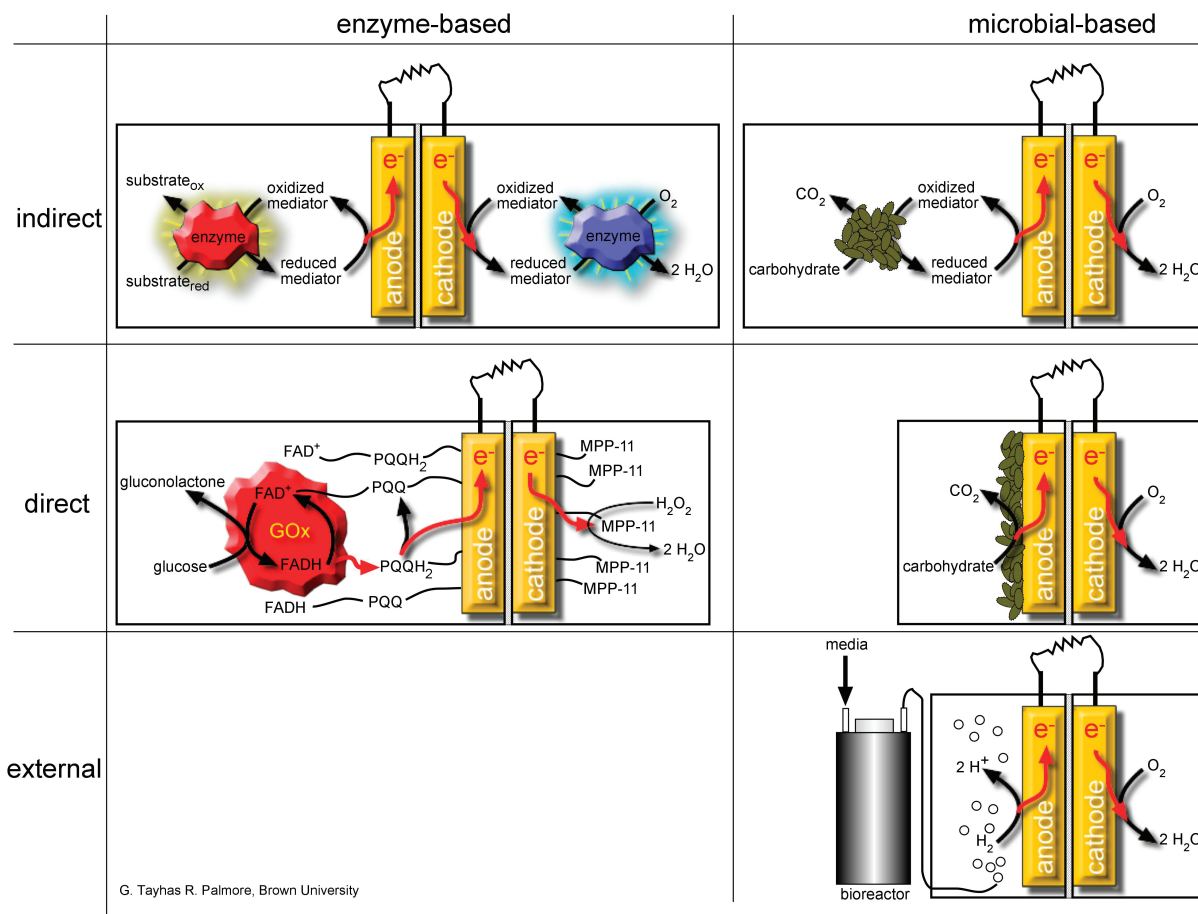


**FIGURE 4.3** A fuel cell converts chemical energy into electrical energy.  $\text{H}_2/\text{O}_2$ : open circuit voltage  $\sim 1.2$  V.  
SOURCE: Image courtesy of G. Tayhas Palmore, Brown University.

<sup>1</sup>I. Willner, E. Katz, F. Patolsky, and A. F. Buckmann. 1998. *Journal of the Chemical Society, Perkin Transactions 2*, 1817-1822.

<sup>2</sup>N. Mano, F. Mao, and A. Heller. 2003. *Journal of the American Chemical Society* 125: 6588.





**FIGURE 4.4** Microbial and Enzymatic Biofuel Cells.  
 SOURCE: Image courtesy of G. Tayhas Palmore, Brown University.

copper (II) to copper (I) with subsequent binding of oxygen to reduce it to water.

Palmore presented some recent examples of simple chemistry done on the surface of proteins that can have a tremendous effect on their overall stability. Jungbae Kim and Jay Grate of Pacific Northwest National Laboratory used simple chemistry to modify lysine residues on enzyme substrates and then tethered them to siloxane, allowing it to gel and harden. This example combines chemistry, nanotechnology, and biotechnology, and shows how chemists can affect how we look at catalysts.

Palmore also talked about examples of microbial systems. Derek Lovley's laboratory at University of Massachusetts, Amherst, is looking at doing electrochemistry in ocean or bay sediments. New organisms are being discovered through their research and the use of a microbial fuel cell in which carbohydrates are taken to carbon dioxide using *Rhodospirillum rubrum* have been demonstrated.

Palmore concluded by highlighting her wish list for future research, which is detailed in chapter 6.

## BIOFUELS FROM BIOMASS INITIATIVES AT DUPONT

**Mark Emptage** of DuPont stated that biomass is the only carbon-based renewable resource for fuel and that there really needs to be a focus on biofuels. However, he believes there is a limit to grain ethanol in the United States, and to produce more ethanol, cellulosics need to be used. Emptage explained that there are many ways of converting biomass to a variety of energy needs. He focused his discussion on hydrolysis of biomass to fermentable sugars and converting the sugars into biofuels. Emptage focused on ethanol, but explained that the technology developed for ethanol can be applied to other fuels as well. He believes biorefining infrastructure should be an add-on to current infrastructure. Next, Emptage discussed the by-products of producing ethanol: The lignin and biomass that result from separating out ethanol can be used as fuel for the entire facility, and the glucose can be used for products other than fuel.

Emptage listed DuPont's guiding principles for cellulosic ethanol process development:

- Keep it simple with minimal unit operations and separations and minimal capital investment.
- Target a single agricultural residue at the beginning (corn stover is the largest source of agricultural residues in the United States).
  - Maximize titer.
  - Life-cycle assessment—need to understand overall process to make it sustainable.
  - Process integration—need to have high efficiency to fit all the pieces together.
  - Risk mitigation—take small steps within the current infrastructure.

Emptage explained the steps involved in converting sugar to ethanol: milling, pretreatments, saccharification, conversion of biomass to fermentable sugars, fermentation, and separation. He said that the key technology is fermentation since it can be applied to butanol or other products. He also explained exactly how corn is harvested and that the two main sugars that can be extracted from biomass are glucan and xylene.

Emptage explained that Dupont is taking a new approach using *Zymomonas mobilis*, a natural ethanol producer found in the sap of agave plants in the tropics. It has a higher yield and productivity than yeast and has the potential to be a better organism than yeast. Emptage announced a collaboration between DuPont and POET, the largest dry-grind producer of ethanol in the United States with over a billion-gallon ethanol capacity. They are working together to develop a pilot plant in South Dakota using the new technology. He said, “This isn’t a revolutionary program. This is really an evolutionary program, just adding on to the current infrastructure.”

Emptage believes that the key remaining challenges are solids handling, having an infrastructure to collect, transport, and store biomass effectively and efficiently with its low-bulk density. Another challenge is the cost of enzymes. The goal is to make the handling of the *Z. mobilis* derived biomass cost competitive with grain ethanol.

## DISCUSSION

**Michael Wasielewski** of Northwestern University asked Thomas Moore about the type of light fluxes being used to investigate the solar flux. He also asked, “Since we all know that photosynthesis has control mechanisms that actually modify electron flow, based on light flux, what kind of prospectus or perspective do we have for control mechanisms in such systems?” Moore explained that one of the factors that seems to limit natural photosynthesis is the diffusion of carbon dioxide into the system for fixing, so it is important in photosynthesis to throttle back the powerful oxidant when carbon dioxide is limiting. There is a control mechanism called nonphotochemical quenching that is related to the

xanthophyll. Moore’s team is working on a model system that responds to high light and quenches excited states releasing the energy as heat, and then as the light intensity comes back down again, the system shuts itself off. He also explained that the system needs to respond to the membrane potential and pH gradient across membranes. This can be done with a potential sensitive sensor.

**R. David Britt** of the University of California, Davis, asked about the limits to purely biological approaches. Thomas Moore said he thinks natural photosynthesis needs to be reengineered to double or triple its power of conversion efficiency. He said that solar will ultimately solve the problem. Moore then called for research focused on fuels by photosynthesis created by cyanobacteria grown on nonarable land and photovoltaics for electricity.

**Douglas Ray** from Pacific Northwest Laboratories asked G. Tayhas Palmore whether the process of engineering enzymes needs to be improved. Palmore said that not much is known about engineering proteins but she hopes that it can be solved using a Brown University database. Mark Emptage said that DuPont has worked with Diversa (non Verenum Corp.), which has put together a set of technologies to allow high-throughput screening and enzyme evolution to be done. He said that there is still a need for more basic understanding about how the enzymes operate on the complex structures.

Charles Dismukes of Princeton asked Mark Emptage how DuPont plans on solving the two major problems that he said need to be addressed: costs for removal of the ethanol distillation and acetic acid inhibition. To solve the first problem, Emptage explained that consolidated bioprocessing will be necessary. That technology has not yet been developed, so it is important to figure out what to do in the near term. DuPont has looked into thermopiles, but they have very low ethanol yields. DuPont is now seeking an organism that maximizes yield, which is why they chose to work with *Zymomonas*. Emptage explained that one way to solve the acetic acid problem is to adjust fermentation conditions to the highest pH level tolerable. DuPont has developed more acetate-tolerant strains. In DuPont’s process with ammonia, acetamide is a by-product with ammonolysis competing with hydrolysis of the acetyl groups, which lowers the total concentration of acetic acid in the process.

Douglas Ray asked whether biobased approaches are going to scale. Emptage said that scaling in fermentation is straightforward, and that tanks can be scaled almost as large as sugar and fermentative organisms. Daniel Nocera of Massachusetts Institute of Technology stated that he is worried about the long-term scaling issue for energy, which is why he supports solar. However, advances in solar energy involve discovery research that is 50 years out. Nocera went on to say that the energy problem is a basic science problem, not an engineering problem, and people should stop focusing on the complex engineering to find a solution.

## 5

# Partnerships and Integration

Workshop organizer Doug Ray remarked at the start of the workshop, that this was an opportunity for participants to reach across disciplines and learn from one another. A number of speakers reiterated similar messages in their talks, and highlighted the need for partnerships, and other efforts that bring different sectors and disciplines together to advance bioinspired chemistry approaches for energy applications. Various speakers and workshop participants presented their thoughts on these needs.

### PARTNERSHIPS

**Brent Erickson** of Biotechnology Industry Organization (BIO) discussed the importance of partnerships among companies. He thinks that large companies with broad skills in biotechnology or those that have good biotechnology partners will capture the full value creation and benefit in the chemicals and fuels markets. Smaller companies, said Erickson, can benefit by partnering with each other or with larger companies, or they can forge strategic partnerships with industrial biotech companies. **Henry Bryndza** of DuPont stressed how important partnerships are for success. For DuPont, there is a complex value chain driven by market disruptions that require partnerships and integrated science approaches to make a difference. He said, “We really need partnerships. . . . We are partnering in virtually all of these areas for a couple of reasons. One is that we can’t do it all ourselves. The second is that in some cases, partners bring market-channel access that we don’t have.”

As discussed in Chapter 2, **Michael Clarke** of the National Science Foundation’s (NSF’s) Chemistry Division talked about an NSF program that forms partnerships in academe. The program was originally called the Chemical Bonding Centers but is now the Centers for Chemical Innovation. NSF makes a number of relatively small awards,

around \$500,000, to fund a group of scientists to collaborate on a major chemistry problem. Harry Gray, Kitt Cummins, Nate Louis, Dan Nocera, and others are working on a project involving the direct conversion of sunlight into fuel. They are in the initial stages of the program and have received about \$500,000 so far. After several years, the research teams can apply for funding up to several million dollars per year.

Brent Erickson of BIO, Henry Bryndza of DuPont, and Mark Emptage of DuPont presented several more examples of projects involving partnerships among and between industry, academe, and national laboratories:

- The company POET is working with Novozymes to develop a no-cook cold enzyme saccharification step that will reduce the amount of energy for conventional ethanol production.
- POET and Ethanex have developed an improved fractionation process so that when corn is ground, a much finer separation of all the different components of the corn kernel results. In combination with the no-cook process fractionation, this leads to a 6 percent increase in ethanol yield. Some of the enzyme hydrolysis waste is put back in the broiler along with the corn stover and cob fiber to generate electricity.
- Cargill has been working on developing a biological route from corn sugar to 3-hydroxypropionic acid (3 HP) for about five years, but could not solve the last step. They then decided to partner with Codexis, which used their metabolic engineering high-throughput screening to figure out how to do it biologically. One of the products of this process is acrylic acid, which is about a \$4 billion global industry. Erickson noted that producing 3 HP from corn sugar is much cheaper and more environmentally friendly than making it from petroleum. Cargill is now working to commercialize this process.



- Cargill and Ashland are going to work together to take the glycerine from biodiesel production in Europe to make propylene glycol.

- DuPont's cellulosic ethanol program is a consortium effort involving other companies, government laboratories, and academia. A wide variety of chemical and biological technologies is being looked at to convert mass into concentrated bio oil. According to Henry Bryndza, DuPont representatives think that the variation in biomass feedstocks is going to require an integration of sciences and multiple technologies.

- An integrated corn biorefinery project has DuPont partnering with Michigan State University, the National Renewable Energy Laboratory (NREL), and Vernium Corp. The project is funded by the Department of Energy using a 50/50 cost-share approach, where companies contribute 50 percent of the funding. Pioneer, a DuPont-owned seed company, and John Deere work on feedstock harvest and transport. Michigan State is working on a life-cycle assessment of farming practices to understand the sustainability of feeding corn stover into the process. DuPont and Vernium are working on developing new enzymes for the hydrolysis of corn stover to fermentable sugars. NREL has developed several technologies for pretreatment with ethanologenic fermentation organisms.

## INTEGRATION AND INTERDISCIPLINARITY

Bryndza thinks the integration of multiple sciences and technologies is necessary. He said that it takes more than biology; chemistry technologies are needed as well as mechanical technologies. Bryndza also believes integration is important in finding the best solution. He thinks that if scientists approach energy problems from either a biological perspective or a chemical perspective, it will not work economically.

During the "Fundamental Aspects" discussion (Chapter 3) **Marcetta Darensbourg** of Texas A&M University said that her team's work could not be done without the help of protein crystallographers. She said that there needs to be support for chemists, biologists, and computational chemists.

Sharon Haynie of DuPont said that it is important not to forget the large infrastructure necessary to reach bioinspired chemistry for energy goals, including analytical, computational, and engineering components. Haynie believes that

an integrative approach is necessary to reach such goals, and that it is important to acknowledge the roles of allies in various scientific and engineering fields.

**Mark Emptage** of DuPont talked about how critical integration is when transferring biomass on the farm to fuels in automobiles. He said that no single company has all the necessary technologies, so it is important to work together.

During the discussion after the "Robust Implementation" session (Chapter 4), **Alex Harris** of Brookhaven National Laboratory discussed integrating both ideas and materials. He believes inorganic concepts need to be integrated with life processes to make energy-producing or conversion schemes work. Harris referred to examples in the presentations that described different approaches of life systems compared with engineered systems in terms of how a charge is transported from one place to another and whether it is stored as chemical energy or transported as charge carriers. He asked, "Are we going to learn from life systems' basic principles of thermodynamics and chemical processes? Is that more likely to be the productive route than to mimic what they're actually doing?" Harris also asked about the challenges in integrating bioinspired systems with inorganic ones. **G. Tayhas Palmore** of Brown University explained that there needs to be an integration of both ideas and materials, and that a multidisciplinary team will help address the challenges presented.

## THE NEED FOR AN HONEST BROKER

During the discussion after the "Industry Perspectives" session (Chapter 2), **Daniel Nocera** of the Massachusetts Institute of Technology highlighted the need for an honest broker. He thinks that scientists can be honest brokers but asked the group to identify an organization that could be an effective, honest broker to guide scientists toward strategic investment.

## DEFINING DISTINCT ROLES

During the discussion after the "Robust Implementation" session (Chapter 4), **Daniel Nocera** declared that academia, national labs, and industry each have their own distinct roles. He said that academics should be working on problems that nobody else wants to work on because there is no financial payback. **Eric Rohlffing** of the Department of Energy talked about how difficult it is for physical scientists to understand biological systems.

## 6

# Research Challenges, Education, and Training

Throughout the workshop presentations and discussions, several participants made suggestions for future research needs and pointed out the funding challenges involved. Participants also identified ways to improve education and training in the area of bioinspired chemistry for energy. This chapter highlights those key points.

### RESEARCH CHALLENGES

During the workshop, various participants made suggestions for future research needs in the area of bioinspired chemistry for energy. Most of the suggestions have been collected and are summarized below in Table 6.1. Further details about these suggestions may be found in the earlier chapters of this workshop summary, or by directly contacting the speakers.

During the discussion after the “Industry Perspectives” session various speakers and workshop participants highlighted funding gaps. Representatives from government agencies discussed current research funding issues. **Eric Rohlifing** of the Department of Energy (DOE) said that the Office of Basic Energy Sciences (BES) could use more money. BES had a major push in fiscal year 2007 for funding fundamental research in solar energy and hydrogen, but it did not come to fruition during the budget cycle. He called for a balance between funding basic research and technology development. **Judy Raper** of the National Science Foundation (NSF) said that her agency does not have enough money in the area of bioinspired chemistry for energy. NSF is a very small funding agency with respect to energy, but it tries to identify new areas of basic science to fund. **John Regalbuto**, director of the Catalysis and Biocatalysis Program at NSF, said that the conversion of biomass to hydrocarbons is poorly funded.

**Charles Dismukes** of Princeton University said that there is a need for adequate funding in the right agencies.

He thinks that DOE should be funding more research in this area. Dismukes also suggested that the money be channeled into agencies that have a peer review process for determining where the funding goes.

**Daniel Nocera** of MIT said that political machines drive funding, and that sometimes, unfortunately, the funding is diverted. He called for an honest broker to keep federal government funding in check. He asked the workshop participants to suggest individuals or organizations that could serve as the most effective honest broker. Eric Rohlifing proposed that the National Academies serve as the honest broker since that is what they are chartered to do.

**Brent Erickson** of BIO presented the current government and commercial funding activities underway for biofuels, biopolymers, and renewable chemicals:

- Congress passed the Energy Policy Act 2005, which is providing a great deal of funding for industrial biotechnology.
- President Bush mentioned cellulosic ethanol during the 2006 State of the Union address, which sent shockwaves through the investment and commercial communities.
- The DOE recently awarded six cellulosic bio-refineries millions of dollars to build on a commercial scale.
- One billion dollars have been provided by venture capital.
- More supportive legislation on funding is coming soon. Senator Bingaman just marked up an energy bill (S.987) that has a large biofuels and cellulosic ethanol component. The House is looking at a similar bill.<sup>1</sup>

<sup>1</sup>As of April 4, 2007, S. 987 was with the Senate Committee on Energy and Natural Resources.

**TABLE 6.1** Future Research Needs

Workshop Participant	Suggestions for Future Research
Peter Preusch National Institutes of Health (Chapter 2)	<ul style="list-style-type: none"> <li>• Address the underlying principles of how to control the metabolism of an organism.</li> <li>• Analyze the complexity of biological systems.</li> <li>• Understand and influence feedback loops.</li> <li>• Understand logic circuits and how best to represent them.</li> </ul>
Brent Erickson Biotechnology Industry Organization (Chapter 2)	<ul style="list-style-type: none"> <li>• Develop technologies that go beyond a simple starch-to-ethanol platform.</li> <li>• Deal with biomass waste using genetically modified organisms.</li> <li>• Address issues regarding the biorefinery infrastructure.</li> </ul>
Magdalena Ramirez British Petroleum (Chapter 2)	<ul style="list-style-type: none"> <li>• Determine what to do with the waste from biorefining and how to innovatively process the final product.</li> </ul>
Daniel Nocera Massachusetts Institute of Technology (Chapter 2)	<ul style="list-style-type: none"> <li>• Solve the multibody problem, a fundamental physics theory for reaction chemistry.</li> <li>• New discoveries in catalysis and new modes of reactivity.</li> <li>• Find new ways to split water.</li> <li>• Discover new fundamental molecular science.</li> <li>• Discover new microbes or thermochemical catalysts for lignin and cellulose conversion</li> </ul>
Michael Wasielewski Northwestern University (Chapter 3)	<ul style="list-style-type: none"> <li>• Need instrumentation allowing mechanistic studies with high-time resolution.</li> <li>• Need systems that provide dynamic detail and mechanistic studies.</li> <li>• Identify more structural changes as a function of time.</li> </ul>
Marcetta Darensbourg Texas A&M University (Chapter 3)	<ul style="list-style-type: none"> <li>• More work on mutations.</li> </ul>
Thomas Rauchfuss University of Illinois, Urbana-Champaign (Chapter 3)	<ul style="list-style-type: none"> <li>• Need for research on bioinspired syngas-like chemistry</li> </ul>
Thomas Moore Arizona State University (Chapter 4)	<ul style="list-style-type: none"> <li>• Engineer a catalyst to break carbon-carbon bonds so that a direct ethanol fuel cell can be developed.</li> <li>• Research focused on fuels by photosynthesis created by cyanobacteria grown on nonarable land and photovoltaics for electricity.</li> <li>• Reengineer photosynthesis to double or triple its power of conversion efficiency.</li> </ul>
G. Tayhas Palmore Brown University (Chapter 4)	<ul style="list-style-type: none"> <li>• Facile expression of enzymes using heterologous hosts.</li> <li>• Truncated enzymes.</li> <li>• Acidophilic and thermophilic organisms and their enzymes in the stabilization of chemistry.</li> <li>• Stabilization of enzymes.</li> <li>• Electroactive nanocomposites.</li> <li>• New redox-active compounds.</li> <li>• Turnover numbers vs. measured current.</li> <li>• Engineered microorganisms.</li> </ul>
Mark Emptage DuPont (Chapter 4)	<ul style="list-style-type: none"> <li>• Basic understanding of how the enzymes operate on complex structures.</li> </ul>

- The upcoming farm bill (H.R. 2419) will have a significant portion dedicated to renewable energy and energy crops.<sup>2</sup>
- There are new federal government policies and funding mechanisms supporting cellulosic ethanol research, development, and commercialization.

During the discussion after the “Fundamental Aspects” session (Chapter 3), **Marcetta Darensbourg** of Texas A&M

University pointed out that it is not enough to fund only chemists. She said that biologists need to be adequately funded as well, and that computational chemistry is also critical to solving the energy problem. .

## EDUCATION AND TRAINING

Workshop speakers and participants indicated ways to improve education and training in the area of bioinspired chemistry for energy, including K-12, undergraduate and graduate education, postdoctoral training, and workforce training.

<sup>2</sup>As of September 4, 2007, H.R. 2419 was received in the Senate.

## K-12 and Undergraduate Education

**John Sheats** of Rider University asked the speakers representing industry and government agencies whether they had plans to support undergraduate students. Brent Erickson responded that his organization supports education for all types of scientists in the biotechnology field. BIO has formed a biotechnology institute in the National Science Teachers Association that does outreach to K-12 education. **Michael Clarke** of NSF said that NSF has been promoting undergraduate research for several years. Programs such as the Research Undergraduate Institution Program comprise both centers and individual research grants for undergraduate institutions. Judy Raper of NSF also pointed out that NSF's engineering division funds K-12 programs as well. Eric Rohlfling said that the DOE's Office of Science has only a modest effort supporting workforce development of teachers and scientists mainly because Congress decided that DOE should not be in the business of education. Rohlfling said that the DOE laboratory system does, however, have a summer internship program for high school teachers. **Peter Preusch** of NIH mentioned the area-grant program, which engages undergraduate institutions through research activities. NIH also awards research education grants to individuals to develop studies on how best to educate students in the areas of science that are relevant to NIH's mission, including chemistry. In addition, NIH's Office of Science Education produces supplemental curriculum materials for K-12.

## Graduate Education

During the discussion after the "Fundamental Aspects" session (Chapter 3), **Thomas Rauchfuss** of the University of Illinois said that his group spends a good amount of money on training students. However, he hopes to receive more funding so that he can provide even better training programs

for his students. Eric Rohlfling said that if energy continues to be a critical issue, scientists who will be working in the chemical industries on energy issues need to be properly trained while in graduate school. **Michael Wasielewski** of Northwestern University pointed out that students currently entering the science and engineering field are aware of the energy problem and appreciate the opportunities that energy research can provide. Students are even asking to work on energy. He is optimistic that educated and qualified students will be able to "carry the ball" into the future.

## Postdoctoral Training

Daniel Nocera brought up the point that NIH is the only federal government agency that funds postdoctoral studies in the United States. He asked the group whether it would be possible to form a national postdoctoral program for students to work on energy research. Eric Rohlfling said that Congress is contemplating such a program, and mentioned the America Competes Act, which includes postdoctoral fellowships in energy. However, Rohlfling also said that DOE does not currently have the resources to support a postdoctoral program. Charles Dismukes stressed how important it is to capture the enthusiasm of students in the field through postdoctoral fellowship programs.

## Workforce Training

During the discussion after the "Industry Perspectives" session (Chapter 2), Daniel Nocera stated that workforce training is critical. Brent Erickson pointed out that there is a shortage of construction firms and trained personnel that can run conventional ethanol plants. Erickson, therefore, called for additional workforce training.



# Appendixes





## Appendix A

### Workshop Agenda

#### MONDAY, MAY 14, 2007

- 8:00 *Introduction*, **Douglas Ray**, Pacific Northwest National Laboratory  
8:15 *Overview*, **John Turner**, National Renewable Energy Laboratory

#### Plenary Session: Federal Government Perspective on Bioinspired Chemistry for Energy

- 8:55 Perspective from DOE Office of Basic Energy Sciences, **Eric Rohlffing**, Department of Energy  
9:10 Developments in BioInspired Chemistry for Energy Systems Funded by the Chemistry Division at NSF, **Michael Clarke**, National Science Foundation  
9:25 Perspective from NSF Division of Chemical, Bioengineering, Environmental, and Transport Systems, **Judy Raper**, National Science Foundation  
9:40 Perspective from NIH National Institute of General Medical Science, **Peter Preusch**, National Institutes of Health

#### Plenary Session: Industry Perspective on Bioinspired Chemistry for Energy

- 10:05 **Henry Bryndza**, DuPont  
10:35 **Brent Erickson**, Biotechnology Industry Organization  
11:05 **Magdalena Ramirez**, BP  
11:35 *Open Discussion*, Sharon Haynie, DuPont (Moderator)

#### Technical Session: Fundamental Aspects of Bioinspired Chemistry for Energy

- 1:30 Hydrogen-processing catalysts for replacement of platinum in fuel cell electrodes: hydrogenases, **Marcetta Darensbourg**, Texas A&M University  
2:00 The Lesson from the Hydrogenases? New Chemistry (Happens to be Strategic), **Thomas Rauchfuss**, University of Illinois at Urbana-Champaign  
2:30 Self-Assembly of Artificial Photosynthetic Systems for Solar Energy Conversion, **Michael Wasielewski**, Northwestern University and Argonne National Laboratory  
3:15 Sustained Water Oxidation by Bioinspired Catalysts: The Real Thing Now, **Charles Dismukes**, Princeton University  
3:45 *Open Discussion*, Sharon Haynie, DuPont (Moderator)  
4:20 *Concluding Remarks*, Sharon Haynie, DuPont

#### Evening Session

4:30-7:30 **Poster Session**

#### TUESDAY, MAY 15, 2007

- 8:00 *Opening Remarks*, **Leonard Buckley**, NRL

#### Plenary Session: Academic Perspective on Bioinspired Chemistry

- 8:05 Solar Fuels: A Reaction Chemistry of Renewable Energy, **Daniel Nocera**, MIT  
8:50 *Open Discussion*

<b>Technical Session: Robust Implementation of Bioinspired Catalysts</b>		10:40	Bioinspired Initiatives at DuPont, <b>Mark Emptage</b> , DuPont
9:25	Mimicking Photosynthetic Energy Transduction, <b>Thomas Moore</b> , Arizona State University	11:10	<i>Open Discussion</i> , Leonard Buckley (Moderator)
9:55	Biological Transformations for Energy Production: An Overview of Biofuel Cells, <b>G. Tayhas Palmore</b> , Brown University	11:40	<i>Concluding Remarks</i> , <b>Leonard Buckley</b> , NRL
		12:00	<i>Workshop Adjourns</i>

## Appendix B

### Biographies

#### ORGANIZERS

**Leonard J. Buckley** as manager of the Materials Chemistry Branch at the Naval Research Laboratory's Chemistry Division, is responsible for guiding research and technology that ranges from fundamental studies in materials synthesis and polymer science to engineering problem solving for U.S. Navy systems. Dr. Buckley was detailed to the Defense Science Office at DARPA in 2001 to manage the Electroactive Polymers Program as well as other efforts involving polymer science and materials chemistry. Dr. Buckley has a doctorate in materials science and engineering from Massachusetts Institute of Technology and a master's degree in polymer science from MIT.

**Sharon L. Haynie** is a research associate at DuPont Biochemical Science and Engineering Group. Haynie earned a B.A. degree in biochemistry from the University of Pennsylvania in 1976 and a Ph.D. in chemistry from MIT in 1982. She began her DuPont career in 1984 in the company's Experimental Station on behalf of the Membrane Scouting Group for Polymer Products after three years with the former AT&T Bell Laboratories. Subsequent assignments included the Vascular Graft Program and the Fibers Department Biomaterials Group. Dr. Haynie has worked the last 10 years in Central Research in the Biochemical Science and Engineering Program, seven years with the groundbreaking bio-3G team. Chair-elect of the Philadelphia Section of the American Chemical Society, she is most proud of her collaborations with multidisciplinary teams of chemists, biologists, and engineers in the quest for new ways to make better products that benefit society.

**Douglas Ray** is the chief research officer at Pacific Northwest National Laboratory (PNNL). He is responsible for

defining and advancing PNNL's science and technology portfolio, coordinating its scientific discretionary investments, providing oversight of the peer-review process at PNNL and its affiliate scientist program, as well as working with counterparts at other DOE laboratories to strengthen the value DOE gets from its national laboratories. A laser spectroscopist, Dr. Ray's research interests are in the effects of weak intermolecular interactions on chemical phenomena in condensed phases, at interfaces, in clusters, and in supramolecular complexes. Dr. Ray received his Ph.D. in chemistry from the University of California, Berkeley. He was a postdoctoral research associate at the Joint Institute for Laboratory Astrophysics, Boulder, Colorado, prior to joining PNNL as a senior research scientist in 1990. He has served in a series of leadership positions in his career at PNNL.

#### SPEAKERS

**Henry E. Bryndza** is the technology director for chemical sciences and engineering in DuPont Central Research and Development. Dr. Bryndza joined DuPont in 1981 and has held a variety of technology, planning, marketing, and business roles. He received his S.B. in chemistry from Massachusetts Institute of Technology, where he conducted research in physical and synthetic organic chemistry with C. G. Swain and D. S. Kemp. He received his Ph.D. in organic chemistry from the University of California, Berkeley, where he did his thesis research on physical organometallic chemistry and catalysis with R. G. Bergman.

**Michael J. Clarke** is the program director for inorganic, bioinorganic and organometallic, chemistry at NSF and holds a permanent position as a professor of chemistry at Boston College. His research focus is on how unusual transition metal ions interact with biological systems. He has

designed and discovered new bioactive metal-containing agents for anticancer and other types of therapy; developed the activation-by-reduction hypothesis for metal anticancer agents; and participated in developing the concept that ruthenium anticancer compounds preferentially enter cancer cells through binding to transferrin. He was among the first to explore how ruthenium complexes bind to DNA and developed some of the early fundamental chemistry of technetium relevant to its use in radioimaging agents. He continues to explore how metal ions affect DNA, RNA, coenzymes, and important sulfur-containing polypeptides such as glutathione. Dr. Clarke is currently interested in how nitrosyl ruthenium compounds can affect the strengthening of neuronal synapses through the release of nitric oxide at the neuronal site.

**Marcetta Y. Darensbourg** received her Ph.D. from the University of Illinois, Champaign-Urbana, in 1967, working with T. L. Brown on organolithium chemistry. Following two years each at Vassar College and SUNY Buffalo, she rose through the academic ranks at Tulane University. During that time, a sabbatical year was spent at Cornell University in the laboratories of Earl Muetterties. In 1982 she and Don Darensbourg moved to Texas A&M University. She has coedited *Experimental Organometallic Chemistry*, an American Chemical Society (ACS) symposium volume, and Volume 32 of *Inorganic Syntheses*. She has served on the ACS Division of Inorganic Chemistry (DIC) governance as chair and also as chair of the Organometallic Subdivision of the DIC. Darensbourg currently serves on three editorial boards: *Inorganic Chemistry*, *Organometallics*, and *Accounts of Chemical Research*. Dr. Darensbourg's awards include the ACS Distinguished Service Award in the Advancement of Inorganic Chemistry, 1996; Association of Former Students (AFS) of Texas A&M Distinguished Teaching Award, 1986 and 2006; AFS Texas A&M Distinguished Research Award, 1995. Her research interests are broadly in inorganic and organometallic reaction mechanisms; and currently, these are applied to bioinorganic systems such as hydrogenase (H<sub>2</sub>ase) enzymes. Synthetic programs are in bioorganometallic chemistry and include synthetic analogues of enzyme active sites such as [NiFe]H<sub>2</sub>ase, [FeFe] H<sub>2</sub>ase, acetyl coA synthase, and nickel superoxide dismutase. She has mentored some 40 graduate students through to the Ph.D. degree.

**G. Charles Dismukes** is professor of chemistry at Princeton University and an affiliated member of the Princeton Environmental Institute and the Princeton Materials Institute. His research interests focus on biological and chemical methods for solar-based fuel production, photosynthesis, metals in biological systems, and tools for investigating these systems. His published works describe the biology and chemistry of oxygen production in natural photosynthetic systems, the synthesis and characterization of bioinspired catalysts for renewable energy production, the use of microorganisms

as cell factories for the production of biofuels, including hydrogen from renewable sources <http://www.princeton.edu/~catalase/>. Dr. Dismukes is principal investigator of the BioSolarH<sub>2</sub> team, a multi-institutional research center focusing on microbial hydrogen <http://www.princeton.edu/~biosolar/>. His independent academic career has been spent entirely at Princeton University, where he currently teaches or coteaches three courses entitled Production of Renewable Fuels and Energy, Astrobiology: Life in the Universe, and the undergraduate chemistry majors laboratory. Dismukes received his Ph.D. in chemistry from the University of Wisconsin-Madison with John Willard, and did postdoctoral work in the Calvin Laboratory at the University of California, Berkeley, with Kenneth Sauer and Melvin Klein.

**Mark D. Emptage** is the biology team leader for the Integrated Corn Biorefinery Program in Central Research and Development at DuPont. He received his Ph.D. in biochemistry from the University of Illinois. He was a post-doctoral fellow in the Enzyme Institute at the University of Wisconsin before joining Central Research at DuPont in 1984. Previous to the biorefinery program Dr. Emptage was a task leader in the development of the PDO biocatalyst that is being used commercially to ferment sugar to BioPDO for DuPont's newest polymer platform, Sorona™.

**Brent Erickson** is executive vice president in charge of the Industrial and Environmental Section at the Biotechnology Industry Organization (BIO). BIO represents more than 1,100 biotechnology companies, academic institutions, state biotechnology centers, and related organizations across the United States and 31 other nations. Mr. Erickson holds a B.S. in biology and an M.A. in international studies. After completing his undergraduate degree, he was involved in fossil fuel research for three years at the U.S. Department of Energy's Laramie Energy Technology Center. After completing graduate school, Mr. Erickson joined the staff of U.S. Senator Alan K. Simpson (R-Wyo.) as a legislative assistant handling energy, public lands, environment, defense and arms control issues. In 1993 Mr. Erickson became legislative director and managed all legislative and policy issues for the senator, who was then the Senate Republican whip. In 1996 Mr. Erickson joined the American Petroleum Institute (API) as a Washington representative and directed government relations efforts on energy and environmental issues. He was chosen to chair a Senate task force of the multiindustry Air Quality Standards Coalition. While at API he earned three special achievement awards. Mr. Erickson joined BIO in 2000 as director of the Industrial and Environmental Section. He was promoted to vice president in 2001 and executive vice president in 2005.

**Thomas A. Moore** is a professor of chemistry and biochemistry at Arizona State University and director of the Center for the Study of Early Events in Photosynthesis

located in the College of Liberal Arts and Sciences. He is the interim director of the Center for Bioenergy and Photosynthesis in the Global Institute of Sustainability at ASU. He was awarded a Chaire Internationale de Recherche Blaise Pascal, Région d'Ile de France, Service de Bioénergétique, CEA Saclay, France, for the period 2005-2007. Professor Moore has a Ph.D. in chemistry from Texas Tech University. He served as president of the American Society for Photo-biology in 2004 and received the Senior Research Award from the Society in 2001. He teaches undergraduate and graduate courses in biochemistry at ASU and lectures in biophysics at the Université de Paris Sud, Orsay. Professor Moore's research in artificial photosynthesis is aimed at the design, synthesis, and assembly of bioinspired constructs capable of sustainable energy production and use.

**Daniel G. Nocera**, the W. M. Keck Professor of Energy at the Massachusetts Institute of Technology, is widely recognized as a leading researcher in renewable energy at the molecular level. Dr. Nocera studies the basic mechanisms of energy conversion in biology and chemistry with primary focus in recent years on the photogeneration of hydrogen and oxygen. The overall reactions require the coupling of multielectron processes to protons and are energetically uphill, thus requiring a light input. He has pioneered each of these areas of science. Most examples of multielectron photoreactions have originated from his research group in the past decade. This work has relied on the generalization of the concept of two-electron mixed-valency in chemistry. He created the field of proton-coupled electron transfer (PCET) at a mechanistic level with the publication of the first ultrafast laser study of an electron transfer through a hydrogen-bonded interface. With the frameworks of multielectron chemistry and PCET in place, Dr. Nocera and his graduate student, Alan Heyduk, described the first molecule to produce hydrogen photocatalytically from homogeneous solutions of hydrohalic acid. Dr. Nocera's research in energy conversion has been featured on the nationally broadcast television programs, ABC Nightline and PBS NOVA in the United States and Explora in Europe. In 2005 he was awarded the Italgas Prize for fundamental contributions to the development of renewable energy at the molecular level.

**G. Tayhas R. Palmore** is a professor of engineering and medical science at Brown University, where she teaches undergraduate and graduate courses in biomaterials and thermodynamics. Dr. Palmore earned her Ph.D. in chemistry from MIT and was a postdoctoral fellow in the Department of Chemistry and Chemical Biology at Harvard University. In 2001, she cofounded the Center for Biomedical Engineering at Brown University, and in 2002 she coestablished the Ph.D. program in Biomedical Engineering. Dr. Palmore has received numerous awards, including postdoctoral fellowships from the National Science Foundation and the Ford Foundation, a CAREER Award from the National Science

Foundation, a Center of Excellence Lectureship from Kyoto University, and a Grass Fellowship from the Radcliffe Institute for Advanced Study at Harvard University. She currently serves on the editorial board of the American Chemical Society journal *Crystal Growth & Design* and is a consultant to industry and government agencies in areas such as biofuel cells, biosensors, batteries, and energy harvesting. Her current research addresses the problem of integrating biology with electronics and energy storage devices from two directions simultaneously: (a) by designing, fabricating, and analyzing operational bioelectronic devices; and (b) by establishing a method for controlling how materials self-assemble.

**Magdalena Ramirez** is the project leader for heavy oil pretreatment processes at British Petroleum (BP) in the United Kingdom. She received her Ph.D. in chemistry from the University of Bath and worked as a senior specialist for emergent technologies at PDVSA-Intevep S.A. for 22 years before joining BP. Ramirez has also been a senior lecturer on technology and innovation management for Universidad Catolica Andres Bello (Venezuela) and a professor in and chair of the chemical engineering faculty of Universidad Central de Venezuela. Her research has touched on many areas, including biocatalysis, adsorbents, selective hydrogenation, and heavy oil upgrading, and has contributed to 130 worldwide patents, 100 published papers, and 120 technical reports.

**Judy A. Raper** is the division director for chemical, bioengineering, environmental and transport Systems (CBET) in the Engineering Directorate of the National Science Foundation. Dr. Raper recently joined NSF after serving as chair of the chemical and biological engineering department at the University of Missouri-Rolla. She is also the former dean of engineering at Sydney University in New South Wales, Australia. Dr. Raper earned a Ph.D. in chemical engineering in 1980 from the University of New South Wales. Her research interests include particle technology, droplets, sprays, aerosols, filtration, and electrostatic effects. Active in scholarship and research, Dr. Raper served as chair for the 4th World Congress on Particle Technology held in Sydney in 2002. Dr. Raper has been involved in policy formation and dissemination and change management at the national level through her work with the Australian Research Council. She is a member of the Particle Technology Forum, associated with the American Institute of Chemical Engineering, and is a fellow of the Institution of Engineers Australia, Institution of Chemical Engineering (United Kingdom), and the Australian Institution of Mining and Metallurgy.

**Thomas B. Rauchfuss** is a professor of chemistry at the University of Illinois at Urbana-Champaign. He received his Ph.D. from Washington State University in 1976. He has studied overseas at the following institutions: the Australian



National University, University of Auckland, University of Strasbourg, and the Technical University of Karlsruhe. Dr. Rauchfuss is interested in all aspects of the synthesis and reactivity of inorganic, organometallic, and main-group compounds and materials. He has received a number of awards for his contributions and is a fellow of both the Royal Society of Chemistry and the Japan Society for the Promotion of Science.

**Eric A. Rohlffing** is the director of the chemical sciences, geosciences and biosciences division in the Office of Basic Energy Sciences (BES), Office of Science, Department of Energy. He received his Ph.D. in physical chemistry from Princeton University in 1982. He held postdoctoral appointments at Exxon Research and Engineering Company and at Los Alamos National Laboratory before joining the staff at the Combustion Research Facility at Sandia National Laboratories in 1986. Rohlffing joined BES in 1997 and served as program manager of the Atomic, Molecular and Optical Sciences Program from 2000 to 2003 and as team leader for Fundamental Interactions from 2003 to the present.

Dr. Rohlffing's research interests include the experimental characterization of transient molecules relevant to combustion processes, linear and nonlinear laser spectroscopies, trace detection of pollutants, molecular beam and mass spectrometric studies of carbon and metal clusters, and vibrational relaxation dynamics. He is the author of approximately 50 peer-reviewed articles, holds membership in the American Chemical Society and the American Physical Society, and is a fellow of the American Association for the Advancement of Science.

**John A. Turner** is a principal scientist at the National Renewable Energy Laboratory. He received his Ph.D. from Colorado State University, and completed a postdoctoral appointment at the California Institute of Technology before joining the National Renewable Energy Laboratory in 1979. His research is primarily concerned with enabling technologies for the implementation of hydrogen systems into the energy infrastructure. This includes direct conversion (photoelectrolysis) systems for hydrogen production from sunlight and water, advanced materials for high temperature fuel cell membranes, and corrosion protection for fuel cell metal bipolar plates. Other work involves the study of

electrode materials for high-energy-density lithium batteries and fundamental processes of charge transfer at semiconductor electrodes. Dr. Turner's monolithic photovoltaic-photoelectrochemical device has the highest efficiency for any direct conversion water splitting device (>12 percent). He has twice received the Midwestern Research Institute President's Award for Exceptional Performance in Research. He has received the Hydrogen Technical Advisory Panel Award for Research Excellence, an Idaho State University Outstanding Achievement Award, and two Outstanding Mentor Awards from the U.S. Department of Energy for his work with undergraduate students. Dr. Turner is the author or coauthor of over 75 peer-reviewed publications in the areas of photoelectrochemistry, fuel cells, batteries, general electrochemistry, and analytical chemistry.

**Michael R. Wasielewski** received his Ph.D. from the University of Chicago in chemistry, where he carried out his graduate research under the guidance of Leon M. Stock. Following his graduate work, he performed postdoctoral research, first with Ronald Breslow at Columbia University and then with Joseph Katz at the Argonne National Laboratory. Subsequently, Dr. Wasielewski joined the scientific staff of the Argonne National Laboratory, where he rose through the ranks to become a senior scientist and group leader of the Molecular Photonics Group. In 1994 Wasielewski joined the faculty of Northwestern University, where he is now professor of chemistry. He served as chair of the chemistry department from 2001 to 2004.

Wasielewski's research interests comprise photoinduced electron transfer and charge transport in organic molecules and materials, artificial and natural photosynthesis, self-assembly of nanoscale materials, spin dynamics of multispin organic molecules, materials for molecule-based optoelectronics and spintronics, and time-resolved optical and magnetic resonance spectroscopy. His research has resulted in over 300 publications. Dr. Wasielewski was elected a fellow of the American Association for the Advancement of Science in 1995, and has held numerous distinguished lectureships and fellowships. Among Wasielewski's recent awards are the 2004 Photochemistry Research Award of the Inter-American Photochemical Society and the 2006 James Flack Norris Award in Physical Organic Chemistry of the American Chemical Society.

## Appendix C

### Poster Abstracts

#### ARTIFICIAL HYDROGENASE SYSTEMS

##### Redox Reactivity of Amine Hydrides of Iridium

Zachariah M. Heiden and Thomas B. Rauchfuss

Department of Chemistry, University of Illinois, Urbana, IL 61801

Metal hydrido-amine complexes (metal = Ru, Rh, and Ir) popularized by Noyori et al. are highly active and enantioselective transfer hydrogenation catalysts. Much of their reactivity beyond use as transfer hydrogenation catalysts remains relatively unexplored. The metal diamido complexes behave as a dehydrogenase-related catalyst toward alcohol/organic substrates. We have found that protonation of the unsaturated diamido derivatives affords an unusual class of soft Lewis acids that will be described. Furthermore, the hydrido-amines act as an oxygenase, and homogeneous fuel cell, catalyzing the unusual reduction of dioxygen with hydrogen similar to knall gas bacteria, resulting in water as the only byproduct.

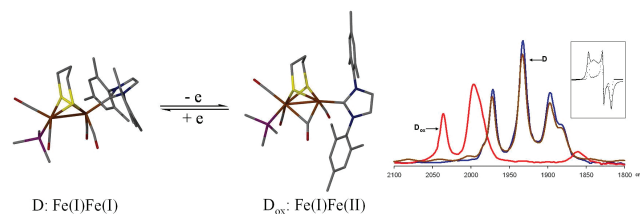
##### Mixed Valent, Fe(II)Fe(I), Diiron Complexes Reproduce the Unique Rotated State of the [FeFe]Hydrogenase Active Site

Tianbiao Liu and Marcetta Y. Darensbourg

Department of Chemistry, Texas A&M University, College Station, TX 77843

The reversible  $\text{Fe}^{\text{I}}\text{Fe}^{\text{I}} \rightleftharpoons \text{Fe}^{\text{I}}\text{Fe}^{\text{II}}$  couple of an N-heterocyclic carbene dinuclear  $\text{Fe}^{\text{I}}\text{Fe}^{\text{I}}$  complex,  $(\mu\text{-pdt})[\text{Fe}^{\text{I}}(\text{CO})_2(\text{PMe}_3)][\text{Fe}^{\text{I}}(\text{CO})_2(\text{IMes})]$  (IMes = 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene), complex **D**, has led to the isolation of the mixed-valent cationic complex **D<sub>ox</sub>** as a biomimetic of the  $2\text{Fe}_2\text{S}$  subsite of the oxidized H cluster in

[FeFe]hydrogenase. This is a rare example of  $\text{Fe}^{\text{I}}\text{Fe}^{\text{II}}$  paramagnetic  $\text{H}_2$ ase model complex studied by X-ray diffraction. As compared with complex **D**, a remarkable reorientation of the IMes NHC ligand enables the  $(\mu\text{-pdt})[\text{Fe}(\text{CO})_2(\text{PMe}_3)][\text{Fe}(\text{CO})_2(\text{IMes})]^+$  cation, **D<sub>ox</sub>**, to exist as a “rotated” structure, with structural and spectroscopic similarities to the diiron unit of  $\text{H}_{\text{as isolated}}$  or  $\text{H}_{\text{ox}}$  (Nicolet et al., 200; Roseboom et al., 2006). The structural makeup of the model includes a Fe-Fe distance that matches that of the enzyme, a semi-bridging CO group, and a pseudo-octahedral iron with open site blocked by a strategically positioned arene group from the bulky NHC carbene ligand (Peters et al., 1998; Nicolet et al., 1999). Other asymmetric disubstituted diiron complexes,  $(\mu\text{-pdt})[\text{Fe}^{\text{I}}(\text{CO})_2(\text{P})][\text{Fe}^{\text{I}}(\text{CO})_2(\text{L})]$  with a selection of P-donor and NHC ligands designed to illustrate the principles that govern stability and function of the  $\text{Fe}^{\text{I}}\text{Fe}^{\text{II}}$  redox level are being studied. The reactivity of the mixed valent  $\text{Fe}^{\text{I}}\text{Fe}^{\text{II}}$  species is being explored.



- (1) Nicolet, Y. L., B. J. Lemon, J. C. Fontecilla-Camps, and J. W. Peters. *Trends Biochem. Sci.* 2000, 25, 138-143.
- (2) Roseboom, W. D. L., A. L. De Lacey, V. M. Fernandez, E. C. Hatchikian, and S. P. J. Albracht, *J. Biol. Inorg. Chem.* 2006, 11, 102-118.
- (3) Peters, J. W., W. N. Lanzilotta, B. J. Lemon, and L. C. Seefeldt, *Science* 1998, 282, 1853-1858.
- (4) Nicolet Y., C. Piras, P. Legrand, C. E. Hatchikian, and J. C. Fontecilla-Camps, *Structure* 1999, 7, 13-23.



### **Toward Understanding the Way Hydrogen Is Formed and Consumed at the Catalytic Center in the Ni-Fe Hydrogenase Enzymes**

Michelle Millar, Dao Nguyen, Harmony Voorhies, and Susan Beatty, Department of Chemistry, SUNY Stony Brook, Stony Brook, New York 11794-3400

The Ni-Fe containing hydrogenases are multicomponent enzymes that catalyze the reversible production and consumption of  $H_2$ . Beyond the biological significance, these enzymes have been heralded as models for potentially low-cost, efficient electrode replacements for the unique Pt electrode systems in fuel cells. We have acquired a number of special nickel-thiolate compounds that replicate some of the unusual structural and electronic and redox properties of the Ni center in hydrogenases, including series of Ni(II), Ni(III) and Ni(IV) redox levels, Ni-H and Ni-CO interactions, as well as Ni-Fe compounds that replicate a portion of the Ni-Fe centers in hydrogenase. Attempts to acquire species that display electrocatalysis will be presented. The ligands developed for this chemistry contain the PS3 and PS2 coordinating entities, as well as related derivatives.

### **New Concepts in Hydrogen Processing: Modeling the Hmd Cofactor and Redox Active Ligands with Platinum Metals**

Aaron Royer, Swarna Kokatam, Zachariah Heiden, Thomas B. Rauchfuss

The enzyme  $H_2$ -forming methylenetetrahydro-methanopterin dehydrogenase, Hmd, is associated with a central step in methanogenesis by Ni-starved archaea. The active site contains an Fe(II) bound organic 3,5-dimethylpyrid-2-one-6-acetic acid group conjugated to a nucleotide. While the Fe complexation in the native enzyme is yet unknown, we have examined the coordination and reactivity of a similar organic ligand, 6-carboxymethyl-4-methyl-2-hydroxypyridine, with  $Cp^*Rh(III)$ . In order to probe the role of the cofactor, dehydrogenation of secondary alcohols and interligand hydrogen bonding will be discussed.

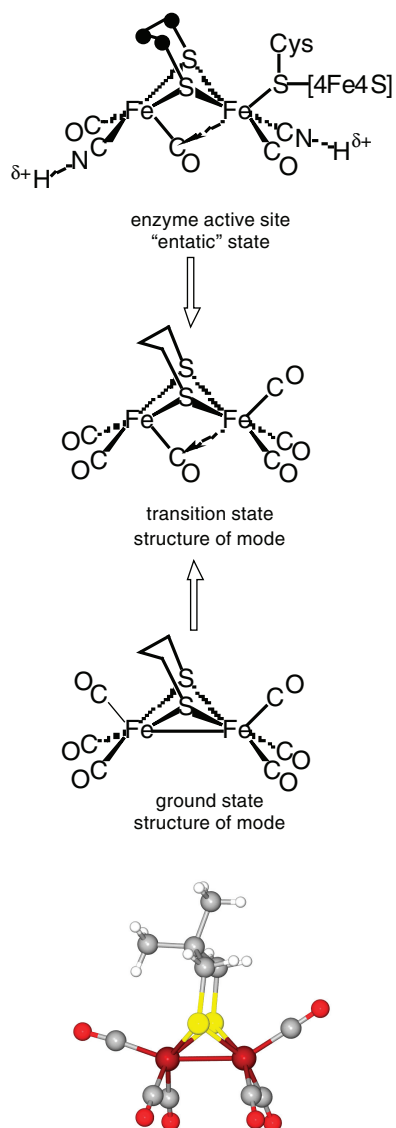
Transition metal ions with organic radicals exist in the active sites of metalloproteins. The best understood example is galactose oxidase, which features a single Cu(II) ion coordinated to a modified tyrosyl radical. Many combined experimental and theoretical studies have focused on electronic properties of metal complexes with redox active ligands, yet reactivity beyond characterization has been limited. We will demonstrate the influence of the metal complex redox state on  $H_2$  activation by anilino-phenolate noninnocent ligands.

### **Biomimetic Efficiency: A Structural and Electronic Investigation of Rotational Barriers Found in DFT-inspired Fe-hydrogenase Models**

Michael Singleton, Roxanne Jenkins, and Marcetta Y. Darensbourg  
Department of Chemistry, Texas A&M University, College Station, TX 77843

While the literature is filled with structural models of Fe-hydrogenases, a truly efficient functional model for the uptake or production of hydrogen gas has yet to be realized. This deficiency is often blamed on the fact that most structural models do not contain the unique "rotated" or entatic state that is the consensus structure of the enzyme active site (*eas*) in its resting state.<sup>1</sup> As demonstrated by  $^{13}C$  VT NMR studies the minimal model of the *eas*,  $(\mu\text{-pdt})[Fe^I(CO)_3]_2$  shows mobility in the  $Fe^I(CO)_3$  units via apical/basal intramolecular CO exchange and in the 3-atom S to S linker.<sup>2</sup> Density functional theory computations have suggested that an electronic effect engendered by the substitution of a CO by a better donor ligand,  $(\mu\text{-pdt})[Fe^I(CO)_3][Fe^I(CO)_2L]$ , lowers the barrier to rotation of the unsubstituted  $Fe(CO)_3$  unit.<sup>3</sup> The computations also suggest that a steric effect in the  $\mu\text{-SRS}$  bridge promotes rotation. In an effort to verify the computational results, we have prepared a series of sterically bulky  $(\mu\text{-SRS})[Fe(CO)_3]_2$  complexes such as the  $(\mu\text{-SCH}_2C(Me)_2CH_2S)[Fe^I(CO)_3]_2$  shown left and characterized them by various X-ray diffraction as well as other spectroscopies, including  $^{13}C$  VT NMR. The prospective application of functional biomimetic models toward the development of cost-effective fuel cells has also led to the evaluation of the all CO compounds as well as the L-substituted derivatives as electrocatalysts for  $H_2$  production.

- (1) Nicolet, Y. L., B. J. Lemon, J. C. Fontecilla-Camps, and J. W. Peters. *Trends Biochem. Sci.* 2000, 25, 138-143.
- (2) Lyon, E. J., I. P. Georgakaki, J. H. Reibenspies, and M. Y. Darensbourg. *J. Am. Chem. Soc.* 2001, 123, 3268-3278.
- (3) Tye, J. W., M. Y. Darensbourg, and M. B. Hall, *Inorg. Chem.* 2006, 45, 1552-1559.



Previous lower-frequency electron spin echo envelope modulation (ESEEM) studies showed a histidine nitrogen interaction with the Mn cluster in the S2 state, but the amplitude and resolution of the spectra were relatively poor at these low frequencies. With the intermediate frequency instruments we are much closer to the “exact cancellation” limit, which optimizes ESEEM spectra for hyperfine-coupled nuclei such as  $^{14}\text{N}$  and  $^{15}\text{N}$ . We will report the results on  $^{14}\text{N}$  and  $^{15}\text{N}$  labeled PSII at these two frequencies, along with simulations constrained by both isotope datasets at both frequencies, with a focus on high-resolution spectral determination of the histidine ligation to the cluster in the S2 state.

### Photochemical Production of Hydride Donor with Ruthenium Complexes with an NAD<sup>+</sup> Model Ligand

Etsuko Fujita,<sup>1</sup> Dmitry Polyansky,<sup>1</sup> Diane Cabelli,<sup>1</sup> Koji Tanaka,<sup>2</sup> and James T. Muckerman<sup>1</sup>

<sup>1</sup>Chemistry Department, Brookhaven National Laboratory, Upton, NY 11973-5000, USA

<sup>2</sup>Institute for Molecular Science and CREST, 5-1 Higashiyama, Myodaiji, Okazaki, Aichi 444-8787, Japan

NAD<sup>+</sup>/NADH is one of the most important redox mediators in biological systems, including photosystem I, and acts as a reservoir/source of two electrons and a proton. A polypyridylruthenium complex with an NAD<sup>+</sup> functional model ligand investigated here is the first example that an NAD<sup>+</sup>/NADH model complex works as a *catalytic hydride donor* for chemical reactions such as the electroreduction of acetone to 2-propanol (Koizumi and Tanaka, 2005). Herein we report clear evidence (Polyanski et al., in press) of photochemical formation of a hydride donor that can transfer a hydride or its equivalent to acetone, and ultimately to C1 species derived from CO<sub>2</sub> reduction as nature does. These results open a new door for photocatalytic hydride (or proton-coupled-electron) transfer reactions originating from metal-to-ligand charge-transfer (MLCT) excited states of metal complexes with a bioinspired NADH-like ligand, and point to a new path for generating fuels from solar energy.

The research carried out at Brookhaven National Laboratory was supported under contract DEAC02-98CH10886 with the U.S. Department of Energy.

## ARTIFICIAL PHOTOSYNTHETIC SYSTEMS

### Multifrequency Pulsed EPR Studies of the Manganese Cluster of PSII

Greg Yeagle, Richard Debus, R. David Britt

We are completing the construction of our CalEPR center at UC-Davis (<http://brittepr.ucdavis.edu>) with five research-grade EPR instruments. Of particular note here are two pulsed EPR instruments working at the intermediate microwave frequencies of 31 and 35 GHz that are providing new high-resolution data on amino acid coordination of the important water-splitting manganese cluster of Photosystem II (PSII).

- (1) Koizumi, T., and K. Tanaka, *Angew. Chem. Int. Ed.* 2005, 44, 5891-5894.
- (2) Polyansky, D., D. Cabelli, J. T. Muckerman, E. Fujita, T. Koizumi, T. Fukushima, T. Wada, and K. Tanaka, *Angew. Chem. Int. Ed.* 2007, in press.

### Pathway to the Artificial Photosynthetic Unit

Elias Greenbaum,<sup>1</sup> Barbara R. Evans,<sup>1</sup> Hugh M. O'Neill,<sup>1</sup> and Ida Lee<sup>2</sup>

<sup>1</sup>Chemical Sciences Division, Oak Ridge National Laboratory

<sup>2</sup>Department of Electrical Engineering, University of Tennessee

A key objective in the field of bioinspired chemistry for energy production is a comprehensive understanding of light-driven electron transfer and the generation of a rational model to serve as a template for future synthetic nanomaterials for solar fuels production. Research at Oak Ridge National Laboratory is aimed at integration of fundamental molecular structural, kinetic, and mechanistic understanding of the conversion of solar energy into chemical energy. The critical science problems of this area of research are the harvesting of solar photons throughout the visible region of the solar emission spectrum and the photocatalytic formation of small fuel molecules, such as hydrogen, methanol, or methane. Using natural photosynthesis as our inspiration combined with biological-synthetic ("soft-hard") catalyst structures, we will couple biomimetic light-activated energetic reactions to nanoscale photocatalytic chemistry to drive the fuel-forming reactions and use water as the source of electrons. This research program will produce the first artificial photosynthetic units and artificial photosynthetic membranes. Success in this area will have a significant impact on the larger picture of a fossil-fuel-free future in which renewable fuels are produced by bioinspired photocatalytic systems.

### Linker Controlled Energy and Charge Sharing Chlorophyll A Assemblies

Richard F. Kelley,<sup>1</sup> Michael J. Tauber,<sup>2</sup> and Michael R. Wasielewski<sup>1</sup>

<sup>1</sup>Department of Chemistry, Northwestern University, 2145 Sheridan Road, Evanston, IL 60208

<sup>2</sup>Department of Chemistry and Biochemistry, University of California, San Diego, CA 92093

The ability of chlorophyll molecules to act as donors and acceptors for both energy and charge transfer in natural photosynthetic systems makes the incorporation of these chromophore/redox centers into artificial photosystems highly desirable. Here we present the first Suzuki and Sonogashira cross-coupling to the 20-meso position of chlorophyll *a*. This methodology was used to rigidly incorporate chlorophyll *a* molecules into several arrays using both covalent and non-covalent interactions. The rigid linkers allow efficient energy transfer among neighboring chlorophylls, efficient charge transfer between chlorophylls in the covalent arrays, and unhindered self-assembly of the arrays in nonpolar media. Small-angle X-ray scattering (SAXS) measurements using the high-flux synchrotron radiation of the Advanced Photon Source at Argonne National Laboratory was used to elucidate the structures of the noncovalent assemblies. The picosecond

lifetimes of energy hopping between chromophores in each array were determined using femtosecond transient absorption spectroscopy. Solution-phase electron paramagnetic resonance (EPR) and electron-nuclear double resonance (ENDOR) studies on chemically oxidized arrays reveal that an unpaired electron is shared between the redox centers in the covalent arrays on a timescale faster than 107 Hz. Future work involves characterization of charge migration in the noncovalently assembled systems.

### Bioinspired Supramolecular Device and Self-Assembly for Artificial Photosynthetic Reaction Center

Oh-Kil Kim,<sup>1</sup> Mike Pepitone,<sup>1</sup> Sungjae Chung,<sup>1</sup> Joseph Melinger,<sup>2</sup> Glenn Jernigan,<sup>2</sup> and Daniel Lowry<sup>3</sup>

<sup>1</sup>Chemistry Division.

<sup>2</sup>Electronics Science & Technology Division.

<sup>3</sup>Center for Biomolecular Science & Engineering, and Institute for Nanoscience

A unique supramolecular device is architected for artificial photosynthetic reaction center based on helical amylose, which is a linear chain polymer of 1,4- $\alpha$  D-glucose and capable of encapsulating various guest molecules as long as the size and interaction forces are compatible with each other. A photo/electro-active donor-acceptor (D-A) pair chromophore is included and rigidified inside the helix, and the helical surface is templated by an array of cyanine dye J-aggregates (super-helix). Such integration of the supramolecular entity occurs by spontaneous self-organization processes in the presence of amylose and the resulting nanodevice becomes water soluble.

A close photonic/electronic communication takes place across the helix between the J-aggregates (antenna) and the chromophore (inside the helix) such that very efficient exciton/electron-transfer proceeds unidirectionally along the helical axis. Energy-transfer (ET) and electron-transfer (eT) from the antenna to D, and from D to A in the confined chromophore, respectively, were investigated based on fluorescence quenching and excited-state lifetime measurements with respect to the helical encapsulation, D-A distance, D/A strength. A remarkably efficient (> 95 percent) ET and eT over D-A distance >20 Å were observed with distinct distance dependence and directionality for the encapsulated chromophores in clear contrast with the encapsulation-free counterparts. It was also found that the helical encapsulation is a powerful means to develop a highly ordered self-assembly of chromophores onto a substrate. This was proved by a fast redox reaction in cyclic voltammetry and oriented thin films often as helical bundles (AFM) upon casting aqueous solution. These were not observable with the encapsulation-free chromophores under the conditions employed.

## Light Energy Conversion by Photosynthetic Proteins at Inorganic Electrodes

Nikolai Lebedev

U.S. Naval Research Laboratory, 4555 Overlook Ave., Washington, DC 20375

The photosynthetic reaction center (RC) is one of the most advanced light-sensing and energy-converting materials developed by nature. Its coupling with inorganic surfaces is attractive for the identification of the mechanisms of interprotein electron transfer (ET) and for the possible applications for the construction of protein-based innovative photoelectronic and photovoltaic devices. Using genetically engineered bacterial RC proteins and specifically synthesized organic linkers, we were able to construct self-assembled and aligned biomolecular surfaces on various electrodes, including gold, carbon, indium tin oxide (ITO), highly ordered pyrolytic graphite (HOPG), and carbon nanotube (CNT) arrays. Our results show that after immobilization on the electrodes, the photosynthetic RC can operate as a highly efficient photosensor, optical switch, and photovoltaic device.

## WATER OXIDATION

### Bioinspired Manganese Complexes for Solar Energy Utilization

Gary W. Brudvig, Sabas G. Abuabara, Clyde W. Cady, Jason B. Baxter, Charles A. Schmuttenmaer, Robert H. Crabtree, and Victor S. Batista

Department of Chemistry, Yale University, PO Box 208107, New Haven, CT 06520-8107

Manganese complexes that catalyze the evolution of oxygen from water, inspired by the oxygen-evolving complex of photosystem II (McEvoy and Brudvig, 2006; Spiviero, et al., 2007), have been extensively investigated by our group (Limburg et al., 1999; Chen et al., 2007). With the goal of using water-oxidation catalysts for solar energy utilization, we have studied the photochemistry of TiO<sub>2</sub> nanoparticles to which a Mn(II)-terpy complex is covalently attached (terpy = 2,2':6,2''-terpyridine). These TiO<sub>2</sub> nanoparticles exhibit visible-light sensitization and charge separation as evidenced by UV-visible, terahertz, and EPR spectroscopy of colloidal thin films and aqueous suspensions. Photoexcitation of [Mn<sup>II</sup>(H<sub>2</sub>O)<sub>3</sub>(catechol-terpy)]<sup>2+</sup>/TiO<sub>2</sub> surface-attached complex leads to Mn(II)→Mn(III) photooxidation within 300 fs, as indicated by terahertz spectroscopic measurements and computational simulations of interfacial electron transfer. The half-time for regeneration of the Mn(II) complex is *ca.* 23 sec (at 6 K), as monitored by time-resolved measurements of the Mn(II) EPR signal. These results are expected to be particularly relevant to photocatalytic applications of Mn(III) complexes, which are known to be effective catalysts

for a wide range of oxidation reactions because Mn(III) is only well known as a stoichiometric oxidant. Our aim is to make the reaction catalytic.

- (1) "Water-Splitting Chemistry of Photosystem II", James P. McEvoy and Gary W. Brudvig (2006) *Chem. Rev.* **106**, 4455-4483.
- (2) "Quantum Mechanics/Molecular Mechanics Structural Models of the Oxygen-Evolving Complex of Photosystem II", Eduardo M. Spiviero, José A. Gascón, James P. McEvoy, Gary W. Brudvig and Victor S. Batista (2007) *Curr. Opin. Struct. Biol.* **17**, 173-180.
- (3) "A Functional Model for O-O Bond Formation by the O<sub>2</sub>-Evolving Complex in Photosystem II", Julian Limburg, John S. Vrettos, Louise M. Liable-Sands, Arnold L. Rheingold, Robert H. Crabtree and Gary W. Brudvig (1999) *Science* **283**, 1524-1527.
- (4) "Speciation of the Catalytic Oxygen Evolution System: [Mn<sup>III/IV</sup>(μ-O)<sub>2</sub>(terpy)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>](NO<sub>3</sub>)<sub>3</sub> + HSO<sub>5</sub><sup>-</sup>", Hongyu Chen, Ranitendranath Tagore, Gerard Olack, John S. Vrettos, Tsu-Chien Weng, James Penner-Hahn, Robert H. Crabtree and Gary W. Brudvig (2007) *Inorg. Chem.* **46**, 34-46.

### Bioinspired Water Oxidation Catalysts for Renewable Energy Production

Greg A. N. Felton,<sup>1</sup> Robin Brimblecombe,<sup>2</sup> Johanna Scarino,<sup>1</sup> John Sheats,<sup>3</sup> Gerhard F. Swiegers,<sup>4</sup> Leone Spiccia,<sup>2</sup> G. Charles Dismukes.<sup>1</sup>

<sup>1</sup>Department of Chemistry and the Environmental Institute, Princeton University.

<sup>2</sup>School of Chemistry Monash University, Australia.

<sup>3</sup>Science Faculty, Rider University.

<sup>4</sup>Division of Molecular Science Commonwealth Scientific and Industrial Research Organisation, Australia.

The capture of light energy to drive water splitting is considered key to future renewable energy production. Studies of the natural photosynthetic water oxidation complex (WOC) of photosystem II (PSII) have led to a series of bioinspired model compounds. These compounds contain [Mn<sub>4</sub>O<sub>4</sub>]<sup>7+</sup> cubic cores. Presently, conditions have been discovered that enable these manganese-oxo cubanes to catalyze the sustained photo-assisted oxidation of water, for several thousand turnovers. These conditions are based on the doping of these cubane compounds into a Nafion<sup>®</sup> film. The properties of these compounds, along with the nature of the conditions use in their incorporation into photoanodes, are being vigorously explored.

### Fine-Tuning the Redox Potential of Mn<sub>4</sub>O<sub>4</sub>L<sub>6</sub> Cubes by Use of Substituted Diarylphosphinic Acids

John E. Sheats,<sup>1</sup> G. Charles Dismukes,<sup>2</sup> Paul Lucuski,<sup>1</sup> Marlena Konieczynska,<sup>1,3</sup> Eric Sellitto,<sup>1,4</sup> Esteban Alverado,<sup>1,3</sup> Matthew Vecchione,<sup>1,4</sup> and Arren Washington<sup>1,4</sup>

<sup>1</sup>Department of Chemistry, Biochemistry, and Physics, Rider University, Lawrenceville, NJ 08648.

<sup>2</sup>Department of Chemistry, Princeton University, Princeton, NJ 08544.

<sup>3</sup>Project SEED Student

<sup>4</sup>Undergraduate Student, Rider University.



Dismukes and coworkers have demonstrated that  $\text{Mn}_4\text{O}_4\text{L}_6$  ( $\text{L}=\text{Ar}_2\text{PO}_2^-$ ), when bound to a Nafion-coated electrode, can oxidize  $\text{H}_2\text{O}$  to produce  $\text{H}_2$  and  $\text{O}_2$  in a catalytic cycle for up to 50,000 turnovers. The voltage required is 1.20 V, the same as needed for photosynthetic oxygen evolution. The Mn cubes have been isolated in four oxidation states:  $\text{Mn}_4(\text{III})\text{4O}_2(\text{OCH}_3)_2\text{L}_6$  to  $\text{Mn}_4(\text{III})(\text{IV})\text{3O}_4\text{L}_6^+$ . The redox potential for the oxidation of  $\text{Mn}_4\text{O}_4\text{L}_6$  ( $\text{L}=(\text{C}_6\text{H}_5)_2\text{PO}_2^-$ ) to  $\text{Mn}_4\text{O}_4\text{L}_6^+$ , 1.20 V, can be reduced by 0.15 V by using  $(4-\text{CH}_3\text{O}-\text{C}_6\text{H}_4)_2\text{PO}_2^-$  and increased substantially by use of  $(3-\text{NO}_2-\text{C}_6\text{H}_4)_2\text{PO}_2^-$ . Experiments are underway to test stronger electron donors such as  $4^-(\text{CH}_3)_2\text{N}-\text{C}_6\text{H}_4$  and  $4^-(\text{C}_4\text{H}_9\text{O}-\text{C}_6\text{H}_4)$  and weaker acceptors such as  $4-\text{CF}_3-\text{C}_6\text{H}_4$  and  $3-\text{Cl}-\text{C}_6\text{H}_4$ . Methods for covalently anchoring the Mn cubes to the surface of an electrode are also being investigated.

## SOLAR CELLS

### Self-Assembled Biomimetic Multifunctional Coatings

Nicholas C. Linn, Chih-Hung Sun, Peng Jiang  
Department of Chemical Engineering, University of Florida,  
Gainesville, FL 32611

We report a simple bioinspired self-assembly technique for fabricating multifunctional optical coatings that mimic both unique functionalities of antireflective motheye and superhydrophobic cicada wing. Wafer-scale, non-close-packed colloidal crystals with remarkably large hexagonal domains are created by a spin-coating technology, which is based on shear-aligning colloidal silica particles suspended in nonvolatile triacrylate monomers. The resulting polymer-embedded colloidal crystals exhibit highly ordered surface modulation and can be used directly as templates to cast poly(dimethylsiloxane) (PDMS) molds. Moth-eye antireflection coatings with adjustable reflectivity can then be molded against the PDMS master. The specular reflection of replicated nipple arrays matches the theoretical prediction using a thin-film multilayer model. The microstructures of the replicated films also lead to the formation of hydrophobic surfaces, even though the native material is inherently hydrophilic. These biomimetic materials are of great technological importance in developing self-cleaning antireflection optical coatings for crystalline silicon solar cells.

### Nanopyramid Arrays for Solar Cells

Chih-Hung Sun, Nicholas C. Linn, Peng Jiang  
Department of Chemical Engineering, University of Florida,  
Gainesville, FL 32611

Current production of solar cells is dominated by crystalline silicon modules; however, due to the high refractive index of silicon, more than 30 percent of incident light is reflected back, which greatly reduces the conversion effi-

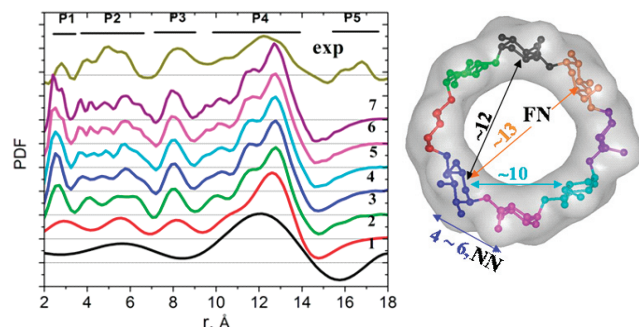
ciency of photovoltaic devices. Surface texturing has become a common practice for Si solar cells and, in combination with vacuum deposited antireflection coatings (ARCs), reduces reflection losses a few percent. Unfortunately, the high cost of vacuum deposition of ARCs is a big challenge for economic production of large photovoltaic panels. Inspired by the antireflection properties of moth eyes, we have developed subwavelength ARCs for crystalline silicon solar cells. Wafer-scale, crystalline arrays of inverted pyramids, which directly function as efficient ARCs, are anisotropically etched in silicon substrates by a cheap yet scalable non-lithographic technique. The inverted pyramid array on Si dramatically reduces the specular reflectivity of the surface and consequently has the potential to increase the conversion efficiency of silicon solar cells.

### X-ray Fingerprinting Bioinspired Supramolecular Structure and Dynamics in Solution

D. M. Tiede,<sup>1</sup> X. Zuo,<sup>1</sup> L. X. Chen,<sup>1</sup> and K. Attenkofer<sup>2</sup>

<sup>1</sup>Chemistry Division and <sup>2</sup>Advanced Photon Source, Argonne National Laboratory, Argonne, Illinois, 60439

Bioinspired, self-assembling supramolecular materials are increasingly being designed for applications in solar energy conversion and storage. However, the dynamic features of these molecular materials typically preclude structural analyses using crystallographic techniques. This makes in situ structural characterization a critical challenge. We have developed techniques that combine wide-angle solution X-ray scattering (WAXS) measured to better than 2 Å spatial resolution with atomistic simulation to provide a new experimental approach for the characterization of supramolecular solution state structure. Comparisons between experimental scattering patterns measured for a range of proteins, DNA, metal coordination complexes, and host-guest assemblies show WAXS and corresponding pair distribution function (PDF) patterns to be sensitive to supramolecular conformation, dynamics, and solvation. For example, a comparison of experimental scattering and PDF patterns for  $\gamma$ -cyclodextrin show features characteristic of the host structure, configurational broadening, and solvation. In current work we are testing the ability of WAXS to serve as a benchmark for quantitative evaluation of molecular dynamics simulations. The ability to provide an experimental marker for supramolecular dynamics and solvation that is directly connected to coordinate models represents a new opportunity for resolving structural dynamics coupled to light-induced charge separation in natural and artificial host matrices. Toward this end we are extending the WAXS technique to include pump-probe techniques at the Advanced Photon Source. Future work is planned for combining 100 ps time-resolved WAXS, X-ray spectroscopy, and magnetic resonance data to achieve a more complete picture of structural reorganization resolved during the time-course of solar energy conversion function.



Experimental PDF measured for  $\gamma$ -cyclodextrin with 1.0 Å spatial resolution (top) compared to PDF calculated from a coordinate model with resolution varying from 6 Å (1) to 0.4 Å (7).

## BIOLOGICAL TRANSFORMATIONS

### Electrobiocatalytic Reduction of $\text{CO}_2$ to Formate: Whole Cell and Isolated Enzyme Systems

Boonchai Boonyaratanakornkit,<sup>1</sup> Rolf J. Mehlhorn,<sup>1</sup> Robert Kostecki,<sup>1</sup> Douglas S. Clark<sup>1,2</sup>

<sup>1</sup>Environmental Energy Technologies Division, Lawrence Berkeley National Laboratory, Berkeley, CA 94720

<sup>2</sup>Department of Chemical Engineering, University of California, Berkeley, CA 94720

Enzymatic reduction of  $\text{CO}_2$  to formate and ultimately to methanol can occur via concurrent electrochemical regeneration of reduced cofactors. By using photovoltaic energy this bioelectrochemical reduction can provide transportable, energy-dense, carbon-neutral liquid fuels. The enzymes involved in fuel production are formate dehydrogenase (FDH) and methanol dehydrogenase, which use the cofactors methyl viologen and pyrroloquinoline quinone (PQQ), respectively. Two issues addressed are the  $\text{O}_2$ -lability of FDH and electron transfer to the enzyme's redox center. Whole-cell biocatalysis is explored by demonstrating that reduced cofactor is permeable to the cell membrane. Cells provide an intracellular environment that stabilizes FDH against  $\text{O}_2$  inactivation. Furthermore, we are connecting FDH to a graphite electrode via a PQQ-FAD linker to enable direct electron transfer from the electrode to the enzyme. This will obviate diffusion of cofactor into the enzyme's redox center and should increase the rate of  $\text{CO}_2$  reduction.

## BIOINSPIRED POLYMERS

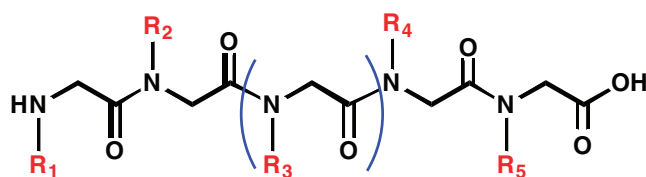
### Bioinspired Polymers for Nanoscience Research

Ronald Zuckermann

Lead Scientist, Biological Nanostructures Facility  
 The Molecular Foundry, Lawrence Berkeley National Laboratory, Berkeley, California

Peptoids are a novel class of non-natural biopolymer based on an N-substituted glycine backbone that are ideally

suited for nanomaterials research. This bioinspired material has many unique properties that bridge the gap between proteins and bulk polymers. Like proteins, they are a sequence-specific heteropolymer, capable of folding into specific shapes and exhibiting potent biological activities; and like polymers, they are chemically and biologically stable and relatively cheap to make. Peptoids are efficiently assembled via automated solid-phase synthesis from hundreds of chemically diverse building blocks, allowing the rapid generation of huge combinatorial libraries. This provides a platform to discover nanostructured materials capable of protein-like molecular recognition and function.



Peptoid Oligomer





## Appendix D

### Workshop Attendees

**Mike Berman**, Air Force Office of Scientific Research,  
Arlington, Virginia

**Carol Bessel**, National Science Foundation, Arlington,  
Virginia

**Boonchai Boonyaratanakornkit**, Lawrence Berkeley  
National Laboratory, Berkeley, California

**R. David Britt**, University of California, Davis

**Gary Brudvig**, Yale University, New Haven, Connecticut

**Louis Brus**, Columbia University, New York

**Henry Bryndza**, DuPont, Wilmington, Delaware

**Leonard Buckley**, Naval Research Laboratory, Washington,  
District of Columbia

**Mark Cardillo**, Camille Dreyfus Foundation, New York

**William Carroll**, OxyChem, Dallas, Texas

**Charles Casey**, University of Wisconsin, Madison

**Alexander Chuang**, Case Western Reserve University,  
Cleveland, Ohio

**Steven Chuang**, University of Akron, Ohio

**Sung-Jae Chung**, Naval Research Laboratory, Arlington,  
Virginia

**Michael Clarke**, National Science Foundation, Arlington,  
Virginia

**Marcetta Darensbourg**, Texas A&M University, College  
Station

**Charles Dismukes**, Princeton University, Princeton,  
New Jersey

**Peter Emanuel**, U.S. Army, Aberdeen Proving Ground,  
Maryland

**Mark Emptage**, DuPont, Wilmington, Delaware

**Brent Erickson**, Biotechnology Industrial Organization,  
Washington, District of Columbia

**Miles Fabian**, National Institutes of Health, Bethesda,  
Maryland

**Greg Felton**, Princeton University, Princeton, New Jersey

**Etsuko Fujita**, Brookhaven National Laboratory, Upton,  
New York

**Louis Graziano**, Rohm and Haas, Spring House,  
Pennsylvania

**Elias Greenbaum**, Oak Ridge National Laboratory, Oak  
Ridge, Tennessee

**Richard Gross**, State University of New York, Brooklyn

**Alex Harris**, Brookhaven National Laboratory, Upton,  
New York

**Sharon Haynie**, DuPont, Wilmington, Delaware

**Zachariah Heiden**, University of Illinois,  
Urbana-Champaign

**Christopher Jarzynski**, University of Maryland, College  
Park

**Wyn Jennings**, National Science Foundation, Arlington,  
Virginia

**Peng Jiang**, University of Florida, Gainesville

**Satya Jujjair**, University of Kentucky, Lexington

**Romas Kazlauskas**, University of Minnesota, St. Paul

**Richard Kelley**, Northwestern University, Evanston, Illinois

**Ray Kellman**, Research Corporation, Tucson, Arizona

**John Kerr**, Lawrence Berkeley National Laboratory,  
Berkeley, California

**Oh-Kil Kim**, Naval Research Laboratory, Arlington,  
Virginia

**Stephen Koch**, State University of New York, Stony Brook

**Walt Kozumbo**, Air Force Office of Scientific Research,  
Arlington, Virginia

**Frederick Krambeck**, ReacTech Inc., Alexandria, Virginia

**Nikolai Lebedev**, Naval Research Laboratory, Arlington,  
Virginia

**Nicholas Linn**, University of Florida, Gainesville

**Jun Liu**, Pacific Northwest National Laboratory, Richland,  
Washington

**Tianbiao Liu**, Texas A&M University, College Station  
**Mary Mandich**, Lucent Technologies, Murray Hill,  
New Jersey

**Michael Maroney**, University of Massachusetts, Amherst

**Luigi Marzilli**, Louisiana State University, Baton Rouge

**Michelle Millar**, State University of New York, Stony Brook

**Raul Miranda**, Department of Energy, Germantown,  
Maryland

**Jin Montclare**, State University of New York, Brooklyn

**Thomas Moore**, University of Arizona, Tempe

**James Muckerman**, Brookhaven National Laboratory,  
Upton, New York

**Dean Myles**, Oak Ridge National Laboratory, Oak Ridge,  
Tennessee

**Janet Nelson**, The National Academies, Washington,  
District of Columbia

**Amar Neogi**, Weyerhaeuser Company, Allentown,  
Pennsylvania

**Kakoli Niyogi**, U.S. Army, Abingdon, Maryland

**Daniel Nocera**, Massachusetts Institute of Technology,  
Cambridge

**G. Tayhas Palmore**, Brown University, Providence,  
Rhode Island

**Josh Peng**, University of Missouri, Kansas City

**Peter Preusch**, National Institutes of Health, Bethesda,  
Maryland

**Stephen Ragsdale**, University of Nebraska, Lincoln

**Magdalena Ramirez**, BP, Middlesex, United Kingdom

**Stephen Rankin**, University of Kentucky, Lexington

**Judy Raper**, Naval Research Laboratory, Arlington,  
Virginia

**Thomas Rauchfuss**, University of Illinois,  
Urbana-Champaign

**Douglas Ray**, Pacific Northwest National Laboratories,  
Richland, Washington

**Charles Riordan**, University of Delaware, Newark

**Michael Rogers**, National Institutes of Health, Bethesda,  
Maryland

**Eric Rohlffing**, Department of Energy, Germantown,  
Maryland

**Aaron Royer**, University of Illinois, Urbana-Champaign

**John Sheats**, Rider University, Lawrenceville, New Jersey

**Mike Singleton**, Texas A&M University, College Station

**Shane Street**, University of Alabama, Tuscaloosa

**Chih-Hung Sun**, University of Florida, Gainesville

**Felicia Taw**, Los Alamos National Laboratory,  
New Mexico

**Levi Thompson**, University of Michigan, Ann Arbor

**Michael Thompson**, Pacific Northwest National  
Laboratories, Richland, Washington

**David Tiede**, Argonne National Laboratory, Illinois

**John Turner**, National Renewable Energy Laboratory,  
Golden, Colorado

**Michael Wasielewski**, Northwestern University, Evanston,  
Illinois

**Rosemarie Wesson**, Naval Research Laboratory,  
Washington, District of Columbia

**Frankie Wood-Black**, ConocoPhillips, Houston, Texas

**Ron Zuckerman**, Lawrence Berkeley National Laboratory,  
Berkeley, California

## Appendix E

# Origin of and Information on the Chemical Sciences Roundtable

In April 1994 the American Chemical Society (ACS) held an Interactive Presidential Colloquium entitled “Shaping the Future: The Chemical Research Environment in the Next Century.”<sup>1</sup> The report from this colloquium identified several objectives, including the need to ensure communication on key issues among government, industry, and university representatives. The rapidly changing environment in the United States for science and technology has created a number of stresses on the chemical enterprise. The stresses are particularly important with regard to the chemical industry, which is a major segment of U.S. industry; makes a strong, positive contribution to the U.S. balance of trade; and provides major employment opportunities for a technical workforce. A neutral and credible forum for communication among all segments of the enterprise could enhance the future well-being of chemical science and technology.

After the report was issued, a formal request for such a roundtable activity was transmitted to Dr. Bruce M. Alberts, chairman of the National Research Council (NRC), by the Federal Interagency Chemistry Representatives, an informal organization of representatives from the various federal government agencies that support chemical research. As part of the NRC, the Board on Chemical Sciences and Technology (BCST) can provide an intellectual focus on issues and fundamentals of science and technology across the broad fields of chemistry and chemical engineering. In the winter of 1996 Dr. Alberts asked BCST to establish the Chemical Sciences Roundtable to provide a mechanism for initiating and maintaining the dialogue envisioned in the ACS report.

The mission of the Chemical Sciences Roundtable is to provide a science-oriented, apolitical forum to enhance understanding of the critical issues in chemical science and technology affecting the government, industrial, and academic sectors. To support this mission the Chemical Sciences Roundtable will do the following:

- Identify topics of importance to the chemical science and technology community by holding periodic discussions and presentations, and gathering input from the broadest possible set of constituencies involved in chemical science and technology.
- Organize workshops and symposiums and publish reports on topics important to the continuing health and advancement of chemical science and technology.
- Disseminate information and knowledge gained in the workshops and reports to the chemical science and technology community through discussions with, presentations to, and engagement of other forums and organizations.
- Bring topics deserving further in-depth study to the attention of the NRC’s Board on Chemical Sciences and Technology. The roundtable itself will not attempt to resolve the issues and problems that it identifies—it will make no recommendations, nor provide any specific guidance. Rather, the goal of the roundtable is to ensure a full and meaningful discussion of the identified topics so that the participants in the workshops and the community as a whole can determine the best courses of action.

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<sup>1</sup>American Chemical Society. *Shaping the Future: The Chemical Research Environment in the Next Century*. American Chemical Society Report from the Interactive Presidential Colloquium, April 7-9, 1994, Washington, D.C.

